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RESEARCHES ON THE COMPLEX INORGANIC ACIDS.[1]

BY WOLCOTT GIBBS, M. D.,
Rumford Professor in Harvard University.

(Continued from Vol. 5, p. 412.)

PHOSPHO-VANADATES.

The existence of a compound of phosphoric and vanadic pentoxides appears to have been first recognised by Berzelius, who regarded it simply as a phosphate of vanadic oxide and ascribed to it the formula $V_2O_3 . 3P_2O_5$, vanadium being then supposed to have the atomic weight 61.5, so that its highest oxide would have the formula V_2O_3. Berzelius describes the supposed salt as lemon-yellow, crystalline, and slowly soluble in water. By dissolving together sodic phosphate and vanadate, adding nitric acid and evaporating at a gentle heat, he obtained a colorless solution which yielded a lemon-yellow salt in large grains made up of fine crystalline needles. For this compound, which he called phosphate of sodium and vanadic acid, he gave no formula. I shall endeavor to show that phosphoric and vanadic oxides unite in various proportions to form well-defined complex inorganic acids, strictly comparable with those which contain phosphoric and molybdic or tungstic oxides.

Phospho-vanadates are formed when alkaline vanadates are heated in contact with free phosphoric acid; when solutions of an

[1] Communicated by the Author, from the Proceedings of the American Academy of Arts and Sciences.

alkaline phosphate are digested with vanadic acid or an acid vanadate; and when alkaline phosphates and vanadates are mixed in presence of a free acid, the conditions being, so far as I have observed, perfectly analogous to those which determine the formation of phospho-tungstates and phospho-molybdates. Phospho-vanadates of the heavy metallic oxides are formed when the divanadates of these oxides are boiled with solutions of alkaline phosphates or with phosphoric acid, and also when the corresponding metallic phosphates are boiled with vanadic acid or acid vanadates. As a rule, the salts are beautifully crystalline, and have a yellow or orange-yellow color, passing in some cases to deep orange-red.

The general characters of the phospho-vanadates are as follows. The alkaline salts have a sulphur-yellow, and in some cases bright yellow color. They are crystalline and often present minute talcose shimmering scales. The relation of these salts to water is especially remarkable. A small quantity of water simply dissolves the phospho-vanadate with a yellow color; on adding more water, the solution gradually becomes orange, then orange-red, and finally deep red. Phosphoric acid is set free, and one or more new definite salts are formed, in which the proportion of the vanadic to the phosphoric oxide is largely increased. Precisely similar changes occur in the action of water upon arsenio-vanadates. When the deep red solutions are evaporated, the changes of color described occur again in the inverse order, and finally the original yellow salt is again obtained, though not always perfectly free from the higher compound. The facility with which the salts of this series are decomposed by water makes it often difficult to obtain them in a state of absolute purity, and renders the reactions with metallic salts uncertain as characteristics. When alkaline phospho-vanadates are evaporated with nitric acid, the base is in many cases entirely separated, and phospho-vanadic acid remains in solution and may separate in crystals. This separation of fixed base often takes place in presence of an excess of phosphoric acid alone. Solutions of alkaline phospho-vanadates appear to be partially reduced by dust or traces of organic matter with exceptional facility. In such cases the solutions take a more or less distinct greenish color, and phospho-vanadico-vanadates are formed. The solutions of these last salts are not very easily oxidised by bromine or nitric acid, and it is therefore advisable

in preparing phospho-vanadates to avoid as much as possible the presence of reducing agents. Alkaline phospho-vanadates dissolve readily in hot solutions of acid tungstates and molybdates, forming orange or orange-red solutions, which yield in many cases beautiful crystalline phospho-vanadico-molybdates and phospho-vanadico-tungstates.

Analytical Methods.—The method usually adopted for the separation of vanadic and phosphoric oxides by means of ammonic chloride may be successfully applied to the analysis of the phospho-vanadates. A small excess of ammonia is to be added to the solution of the salt, which is then to be heated until it becomes colorless. In this manner we obtain a simple mixture of phosphate and metavanadate. Ammonic chloride is then to be added, and the analysis conducted in the usual manner. This method permits the separate determination of each of the pentoxides and so far offers an advantage. On the other hand, it only applies to salts with alkaline bases. It is far more convenient, and at least equally accurate, to determine the vanadium by titration with hypermanganate under appropriate conditions. The end reaction is usually well defined in a sufficiently dilute solution. The sum of the vanadic and phosphoric oxides may be accurately determined by precipitating the solution of the two pentoxides at a boiling heat by means of mercurous nitrate, adding mercuric oxide until a small but distinct excess is present so as to perfectly neutralise the free acid, and then boiling for a few minutes. Since the ignited mass of oxides retains mercuric oxide with some tenacity, it is best, after burning off the filter with a very free access of air, to add a weighed portion of sodic tungstate and ignite until a constant weight is obtained. When the process is carefully conducted, the fused mass contains all the phosphoric oxide and all the vanadium as pentoxide. Care should be taken to oxidise the whole of the vanadium to pentoxide as more certain. Any small quantity of dioxide present is, however, precipitated when an excess of mercuric oxide is present. This method applies to all salts or compounds containing oxides of phosphorus and vanadium. As regards the details of the determination of vanadium by titration with potassic hypermanganate the following points require attention.

For the reduction of vanadic pentoxide to dioxide, it is best, after adding dilute sulphuric acid, to boil with a solution of sulphurous acid and afterward to evaporate the solution nearly, at

least, to dryness upon a water-bath, so as to insure a perfect reduction and at the same time to expel the last traces of sulphurous oxide. Sulphydric acid gas also readily reduces the vanadic pentoxide in presence of sulphuric acid, but there is almost always a separation of free sulphur in a state of extreme subdivision. This passes readily through the filter, and the results of the titration are not so satisfactory as when sulphurous acid is employed as the reducing agent. The solution of vanadic dioxide should be diluted till the color is pale blue, heated to about 80°–100°, and titrated hot. In the hot solution the disappearance of the hypermanganate takes place instantly, and the end reaction is much more quickly and satisfactorily attained. The actual results are precisely the same as when a cold solution is employed, as the following titrations sufficiently prove.

I. In a cold solution of VO_3 in SO_4H_2 three successive portions of 200 cc. each required 4.62 cc., 4.64 cc., and 4.63 cc. of hypermanganate solution.

II. At 53° C. 200 cc. as before required 4.62.

III. At 62° C. 200 cc. required 4.66 cc. Process rather more rapid.

IV. At 70° C. 200 cc. required 4.66 cc. Process rather more rapid.

V. At 80° C. 200 cc. required 4.65 cc. Color vanished instantly.

VI. At 100° C. 200 cc. required 4.64 cc. Color vanished instantly.

The following analyses will show the effect of reducing by hydric sulphide, as compared with reduction by sulphurous acid. In an acid sodic vanadate:

I. 0.0908 gram gave 0.0466 gram V_2O_5 = 44.67 per cent. with H_2S.

II. 0.1381 gram gave 0.0607 gram V_2O_5 = 43.92 per cent. with H_2S.

III. 0.1540 gram gave 0.0692 gram V_2O_5 = 44.90 per cent. with H_2S.

IV. 0.1625 gram gave 0.0696 gram V_2O_5 = 42.99 per cent. with SO_2H_2.

V. 0.1532 gram gave 0.0659 gram V_2O_5 = 43.01 per cent. with SO_2H_2.

When hydric sulphide is used as a reducing agent, it often happens that the filtrate on evaporation deposits more sulphur. In titrating with hypermanganate, the final color reaction must be

permanent for ten to fifteen minutes at least. As usual, the amount of hypermanganate required to color an equal volume of water and dilute sulphuric acid must be determined, and the proper correction applied.

In my paper on the vanadio-molybdates I have given another method of determining vanadium based upon the fact that a ferrous salt readily reduces vanadic pentoxide in the presence of free chlorhydric acid. I have since found that this method is not new, but was proposed and tested by Otto Lindemann[1] some years since.

1 : 1 *Ammonic Phospho-vanadate.*—When any ammonic vanadate is dissolved with an excess of ammonic phosphate, and nitric acid is cautiously added in small quantities at a time, a deep orange-red solution is obtained, which on heating becomes colorless, but which on evaporation to a small volume yields beautiful bright yellow granular crystals. These are to be carefully washed with cold water, in which they are not very soluble. The solution has at first a fine yellow color, but on continued dilution with water passes through the changes in color which have already been described. In this salt,

0.5582 gram lost on ignition with WO_4Na_2 0.1017 gram = 18.22 per cent.

0.7667 gram lost on ignition with WO_4Na_2 0.1393 gram = 18.17 per cent.

0.5329 gram gave 0.0707 gram $(NH_4)_2O$ = 13.28 per cent.

0.9753 gram gave 0.4501 gram V_2O_5 with $KMnO_4$ = 46.15 per cent.

0.6883 gram gave 0.3174 gram V_2O_5 with $KMnO_4$ = 46.13 per cent.

0.1073 gram gave 0.0495 gram V_2O_5 with $KMnO_4$ = 46.15 per cent.

The analyses lead to the formula

$$P_2O_5 . V_2O_5 . (NH_4)_2O + Aq,$$

which requires :

		Calc'd.	Mean.
P_2O_5	142	35.99	35.67
V_2O_5	182.6	46.27	46.14
$(NH_4)_2O$	52	13.17	13.28
H_2O	18	4.57	4.91
	394.6	100.00	

[1] Ueber die quantitative Bestimmung des Vanadins. Inaugural Dissertation von Otto Lindemann. Jena, 1879.

I have here assumed that the simplest expression of the results of the analyses represents the molecular weight. It will, I think, appear from the study of other compounds, that it is at least probable that the molecular weight is much higher. The solution of the salt is very easily reduced by dust or traces of organic matter. The solution then contains a greater or less proportion of a phospho-vanadico-vanadate. The solution of the salt has a yellow color and a very strong acid reaction, but this probably depends simply upon the decomposition which sets phosphoric acid free.

1 : 1 *Argentic Phospho-vanadate.*—A quantity of the above-described ammonium salt was dissolved with ammonic phosphate, and argentic nitrate added to the solution in excess. A sulphur-yellow crystalline precipitate was at once formed, which was digested with very dilute nitric acid so as to remove argentic phosphate, and then presented granular yellow crystals but slightly soluble in cold or hot water. The salt is readily decomposed by dilute chlorhydric acid, and then yields a yellow solution which is probably the acid of the series. In the silver salt,

1.4134 gram gave 0.9192 gram AgCl = 52.59 per cent. Ag_2O.

1.6267 gram gave 0.7938 gram metallic silver = 52.41 per cent. Ag_2O.

1.3696 gram gave 0.2851 gram V_2O_5 = 20.82 per cent.

1.0193 gram lost on ignition 0.1067 gram = 10.47 per cent.

The analyses lead to the formula

$$P_2O_5 . V_2O_5 . 2Ag_2O + 5Aq,$$

which requires :

		Calc'd.	Found.	
P_2O_5	142	16.19	16.21	
V_2O_5	182.6	20.83	20.82	
$2Ag_2O$	464	52.70	52.59	52.41
$5H_2O$	90	10.28	10.47	
	478.6	100.00		

6 : 4 *Potassic Phospho-vanadate.*—When ammonio-magnesic phosphate, $P_2O_5Mg_2(NH_4)_2$, is boiled with a strong solution of potassic divanadate, the phosphate disappears and is replaced by yellow granular masses, which are but slightly soluble in water. In this salt, after washing with cold water,

0.5401 gram gave 0.3852 gram P_2O_5 and V_2O_5 = 71.31 per cent.

0.3790 gram gave 0.1777 gram V_2O_5 with $KMnO_4$ = 46.89 per cent.

0.3790 gram lost on ignition (alone) 0.0619 gram = 16.31 per cent.

The analyses lead to the formula

$$4P_2O_5 . 6V_2O_5 . 3K_2O + 21Aq,$$

which requires:

		Calc'd.		Found.	
$4P_2O_5$	568	24.41	71.59	24.42	71.31
$6V_2O_5$	1098	47.18		46.89	
$3K_2O$	283	12.16	28.41	12.38	28.69
$21H_2O$	378	16.25		16.31	
	2327	100.00			

No magnesium and no ammonium could be detected in the salt, and it seems at least probable that the salts of the series might be prepared by the same process, other acid vanadates being substituted for the potassic salt employed. A strong solution in cold water gave a brick-red fine granular precipitate with argentic nitrate, and yellow flocky precipitates with mercurous and thallous nitrates. The mercurous precipitate was distinctly seen to contain two different compounds, and it is therefore probable that the potassic salt was decomposed even by a small quantity of cold water.

7 : 6 *Hydric Phospho-vanadate.*—When a solution of phosphoric acid is mixed with a strong solution of sodic divanadate, a yellow uncrystalline mass is formed. This after standing some days becomes distinctly crystalline, and may be washed with cold water until the washings become orange-red. In a preparation of this salt, dried as usual upon woollen paper,

1.2172 gram gave 0.4846 gram V_2O_5 = 39.81 per cent.

0.8553 gram gave 0.6487 gram mixed oxides = 75.84 per cent. $P_2O_5 + V_2O_5$.

0.6127 gram lost with WO_4Na_2 0.1470 gram = 24.00 per cent. water.

The analyses show that the compound analysed contained no soda, and that it is a 7 : 6 phospho-vanadic acid, the formula of which may be written

$$7P_2O_5 . 6V_2O_5 . 3H_2O + 34Aq.$$

The formula requires:

		Calc'd.		Found.	
$7P_2O_5$	994	39.76	75.83	39.81	75.84
$6V_2O_5$	1096	36.07		36.03	
$37H_2O$	666	24.17		24.00	
	2756	100.00			

The sum of the phosphoric and vanadic oxides found by difference is 76.00. After all saline matters are washed out, the acid dissolves readily in water, and gives an orange solution, which changes color on dilution in the manner already explained. I shall, after describing the phospho-vanadico-vanadates and arsenio-vanadico-vanadates, return to this and the preceding compounds.

20 : 1 *Phospho-vanadic Acid.*—When the solution of phosphoric acid is mixed with one of ammonic metavanadate, the liquid becomes orange, but after heating for a time upon a water-bath lemon-yellow, and then deposits a large quantity of a lemon-yellow crystalline salt. More of this salt is deposited on evaporating the mother liquor, and again after partially neutralising with ammonia. The yellow salt may be drained with the filter-pump and then washed with a small quantity of cold water. The salt presents fine yellow crystals, which dissolve in a small quantity of hot water. The liquid is at first yellow, but on adding more hot water, and especially on heating, it becomes orange; with more water, orange-red, and finally deep garnet-red with a very strong acid reaction. If this solution is evaporated upon a water-bath the changes of color occur in the inverse order; that is to say, the liquid gradually becomes orange-red, orange, and yellow, and the original salt is finally deposited. The changes of color observed are due to the decomposition of the ammonium salt by water, and the formation of ammonic phosphates and of phospho-vanadates differing in constitution from the original compound and containing a greater proportion of vanadic pentoxide for one molecule of phosphoric oxide. Phosphoric acid is also set free in the reaction. The deep red solution, on standing, deposits beautiful small granular ruby or garnet-red crystals. Of these crystals,

0.3156 gram lost on ignition (alone) 0.0691 gram = 21.89 per cent.

0.3156 gram gave with $KMnO_4$ 0.2377 gram = 75.32 per cent.

The analyses correspond with the formula

$$20V_2O_5.P_2O_5.6H_2O + 53Aq,$$

which requires:

		Calculated.	Found.
$20V_2O_5$	3660	75.24	75.32
P_2O_5	142	2.92	2.79
$59H_2O$	1062	21.84	21.89
	4864	100.00	

The phosphoric oxide was determined by the difference. The solution of the acid has a dark red color and a strongly acid reaction. It gives cinnamon-colored flocky precipitates with nitrates of silver and thallium. The silver salt is readily decomposed by potassic chloride in presence of a trace of chlorhydric acid, giving a red solution which deposits beautiful square thin tabular crystals, the red color of which is so deep that they appear black by reflected light. In preparing the salts of this series, it will probably be best to saturate a small proportion of the acid with an alkaline base, and then to add the rest of the acid. For the present the basicity of the acid is undetermined, and the assumption that it contains six molecules of water is merely provisional. It also appears probable that salts of this and similar higher series may be prepared by mixing solutions of alkaline metavanadates with those of alkaline phosphates in definite proportions, and then adding dilute sulphuric acid in small portions at a time, stirring or shaking after each addition of acid. The precise quantity of acid to be added should be calculated beforehand, which may of course be easily done if we assume a definite basicity, as, for instance, that each molecule of salt shall contain three molecules of fixed base.

PHOSPHO-DIVANADATES.

The salts of this series are formed under conditions which have already been pointed out. They have frequently, at least, a fine yellow color, and are decomposed by water with formation of salts of other series.

Phospho-divanadate of Ammonium.—This is the yellow crystalline salt referred to as formed by the action of phosphoric acid upon ammonic metavanadate. The salt dissolves in a small quantity of cold water without apparent decomposition, but the reactions

of the solution are at best rather uncertain. Argentic nitrate gives a fine bright yellow crystalline precipitate. In the ammonium salt,

1.1259 gram lost on ignition 0.2876 gram = 25.54 per cent. NH_3 and H_2O.

1.0600 gram lost on ignition with WO_4Na_2 0.2723 gram = 25.69 per cent.

1.0624 gram gave 0.1676 gram NH_4Cl = 7.67 per cent $(NH_4)_2O$.

1.4112 gram gave 0.7534 gram V_2O_5 = 53.40 per cent.

The analyses lead to the formula

$$P_2O_5.2V_2O_5.(NH_4)_2O.2H_2O + 5Aq,$$

which requires:

		Calculated.	Found.
P_2O_5	142	20.74	20.98 (diff.)
$2V_2O_5$	365	53.28	53.40
$(NH_4)_2O$	52	7.59	7.67
$7H_2O$	126	18.39	17.95
	685	100.00	

The formula given corresponds to the provisional assumption of three molecules of water in the acid.

ARSENIO-VANADATES.

These salts are formed under precisely the same conditions as those which determine the formation of phospho-vanadates. The general characters of the salts are almost precisely similar. Like the phosphorus compounds, they are yellow or orange-yellow and crystalline. They are decomposed by water, and yield deep orange-red salts of new series, in which the proportion of vanadic to phosphoric oxide is largely increased.

Analytical Methods.—Arsenic is most conveniently determined in these salts by reduction with sulphurous acid and precipitation of arsenious sulphide by sulphydric acid. The sulphide is then to be weighed upon an asbestos filter. In the filtrate, which contains the vanadium as dioxide, the vanadic pentoxide may be determined by potassic hypermanganate. Dilute sulphuric acid is to be added in place of chlorhydric acid before precipitation with sulphydric acid. Water cannot be accurately determined in these salts by ignition with sodic tungstate, as a greater or less quantity of arsenic oxide is always volatilised. The best method consists in cautiously

heating the salt over a radiating cup of sheet-iron until a constant weight is obtained.

5 : 8 *Arsenio-vanadic Acid.*—When sodic divanadate and arsenate are dissolved together in boiling water, and nitric acid is added in small portions at a time, a deep orange liquid is obtained which on evaporation to dryness upon a water-bath yields an orange-yellow crystalline mass. This is to be purified by careful washing with cold water, when a beautiful crystalline orange-colored salt remains. The salt is somewhat soluble in cold, and readily in hot water. The solution is very easily reduced by dust or other organic matters, and becomes greenish-orange with formation of a greater or less quantity of an arsenio-vanadico-vanadate. It is then difficult to reoxidise the solution so as to obtain the original compound. On analysis,

{ 0.8558 gram gave 0.3374 gram As_2S_3 = 36.87 per cent. As_2O_5.
{ 0.8558 gram gave 0.4058 gram V_2O_5 with $KMnO_4$ = 47.41 per cent.

0.8715 gram lost over a radiator 0.1358 gram = 15.58 per cent.

The analyses correspond to the formula

$$5As_2O_5.8V_2O_5.3H_2O + 24Aq,$$

which requires:

		Calculated.		Found.	
$5As_2O_5$	1150	47.18 }	84.31	47.41 }	84.28
$8V_2O_5$	1461	37.13 }		36.87 }	
$27H_2O$	486	15.69		15.58	
	3097	100.00		99.86	

The water, as estimated by difference, amounts to 15.72, so that the direct determination is nearly correct, and no fixed base is present. In a second preparation, in which I employed residues containing arsenic and vanadium from the preparation of the arsenio-vanadico-vanadates to be described and oxidised with nitric acid and potassic hypermanganate, I found the ratio of the arsenic to the vanadic oxide to be as 7 : 6.

{ 1.2105 gram gave 0.5825 gram As_2S_3 = 44.99 per cent. As_2O_5.
{ 1.2105 gram gave 0.3748 gram V_2O_5 = 30.97 per cent.

The difference here cannot be taken as water, as some manganous oxide was present; but the acid may, like the corresponding phosphorus compound, be regarded as

$$7As_2O_5.6V_2O_5.3H_2O.$$

Since the publication of the preliminary notice in which I announced the discovery of this class of compounds,[1] and threw the whole subject open to chemists, a short paper has appeared by F. Fernandez,[2] in which the writer describes an arsenio-vanadate of ammonium, which, except so far as water of crystallisation is concerned, corresponds to the ammonic phospho-vanadate which I have described, so that we now have

$$P_2O_5.V_2O_4.(NH_4)_2O + Aq,$$
$$As_2O_5.V_2O_5.(NH_4)_2O + 11Aq.$$

Want of material has prevented a more complete study of the subject on my own part.

PHOSPHO-VANADICO-VANADATES.

The salts of this series are very readily formed by boiling an excess of a mixture of vanadic dioxide and pentoxide with alkaline phosphates, when the mixed oxides dissolve to form red or greenish-red solutions, which on cooling yield in many instances very beautiful crystalline salts. The same result is obtained by fusing the mixture of oxides obtained by igniting ammonic metavanadate with alkaline phosphates; by partially reducing phospho-vanadates, or by adding solutions of vanadic dioxide to solutions of phospho-vanadates. The alkaline phospho-vanadico-vanadates are often very beautiful, and present extremely well-defined crystals. They have usually a green color, which may be so deep as to appear black in large crystals. By oxidation they pass into phospho-vanadates.

Analytical Methods.—These are the same as those described for the analysis of phospho-vanadates. The vanadic dioxide may be determined directly by titration with potassic hypermanganate in dilute solutions containing free sulphuric acid. In another portion of the solutions the vanadic pentoxide is to be reduced with sulphurous acid, and then determined by titration. The whole quantity of oxides may be found by mercurous nitrate and mercuric oxide after completely oxidising the vanadic dioxide with nitric acid.

18:1:2 *Phospho-vanadico-vanadates of Ammonium.*—When a solution of phospho-vanadate of ammonium is mixed with one of

[1] This Journal **4**, 577.

[2] Berichte der deutschen chem. Gesellschaft **17**, 1632. July, 1884.

vanadic dioxide in chlorhydric acid, and the liquid is allowed to stand for some time, beautiful deep green prismatic crystals are deposited. These dissolve in hot water to a very deep red solution, and appear to be decomposed exactly in the manner which has been explained in the case of the phospho-vanadates. Of this salt,

0.3647 gram lost on ignition with WO_4Na_2 0.0938 gram = 25.72 per cent.

0.5318 gram gave 0.3657 gram V_2O_5 and P_2O_5 = 68.76 per cent.

0.4958 gram gave 0.0084 gram VO_2 with $KMnO_4$ = 1.68 per cent.

0.4958 gram gave 0.0083 gram VO_2 with iodine and CO_3NaH = 1.69 per cent.

0.4284 gram gave 0.0325 gram $(NH_4)_2O$ = 7.59 per cent.

The vanadic dioxide was oxidised with nitric acid before precipitation with mercurous nitrate and mercuric oxide. The resulting percentage is to be corrected accordingly. The analyses correspond fairly well with the formula

$$18V_2O_5.VO_2.2P_2O_5.7(NH_4)_2O + 50Aq,$$

which requires:

		Calculated.	Found.	
$18V_2O_5$	3294	66.88	67.08	
VO_2	83	1.69	1.68	1.74
$2P_2O_5$	284	5.77	5.51	
$7(NH_4)_2O$	364	7.39	7.59	
$50H_2O$	900	18.27	18.13	
	4925	100.00		

The phosphoric oxide is determined by difference only. The compound may also be regarded as a double salt; as, for instance,

$$6V_2O_5.VO_2.3(NH_4)_2O + 2[6V_2O_5.P_2O_5.2(NH_4)_2O.H_2O] + 48Aq;$$

but we have at present no data for deciding the question. The solution in cold water gives brown flocky precipitates with salts of silver and thallium and with mercurous nitrate, none with baric chloride at first, but after a short time the mixture becomes turbid and then deposits distinct orange crystals mixed with a brown flocky matter. The salt is therefore probably decomposed by solution.

4:5:1 *Phospho-vanadico-vanadate of Sodium.*—A boiling solution of sodic orthophosphate dissolves the mixture of vanadic oxides obtained by igniting ammonic metavanadate, and gives a greenish liquid which on cooling deposits green crystalline scales with a talcose lustre. The same salt is formed by fusing together the mixed oxides and sodic phosphate, but is in this way more difficult to obtain in a state of purity. The compound is insoluble in water, and cannot therefore be purified by recrystallisation. Of this salt,

1.4264 gram lost on ignition 0.3904 gram = 27.37 per cent. water.

1.2893 gram gave 0.8136 gram $V_2O_5 + P_2O_5 = 63.10$ per cent.

1.7149 gram gave 0.5815 gram V_2O_5 by titration with $KMnO_4$ = 33.90 per cent.

1.4190 gram gave 33.67 per cent. and 33.75 per cent.

—— gram gave 3.11 per cent. VO_2.

The analyses correspond tolerably well with the formula

$$5P_2O_5.4V_2O_5.VO_2.4Na_2O + 37Aq,$$

which requires:

		Calculated.	Found.
$5P_2O_5$	710	29.11	29.15 29 32 (diff.)
$4V_2O_5$	732	30.01	30.66
VO_2	83	3.40	3.11
$4Na_2O$	248	10.17	9.74
$37H_2O$	666	27.31	27.17
	2439	100.00	

12:12:6 *Potassic Phospho-vanadico-vanadate.*—When solutions of potassic divanadate and potassic orthophosphate, PO_4K_2H, are heated together, the phosphate being in large excess, a colorless solution is formed. A solution of vanadic dioxide in a large excess of chlorhydric acid then often produces almost immediately a precipitate of black granular crystals. In some cases, however, the black salt is formed only after standing some hours. Under the microscope the black crystals appear to be cubes, though this is rather uncertain. The true color is deep green. The salt is insoluble in water containing other saline bodies; but as soon as the crystals are completely washed, they dissolve readily in hot water with decomposition, a beautiful green salt crystallising from the solution on standing. Of the black crystals,

0.4978 gram lost with WO_4Na_2 0.0716 gram = 14.38 H_2O.

0.1622 gram gave with $KMnO_4$ 0.03177 gram VO_2 = 19.59 per cent.

0.1201 gram gave with $KMnO_4$ 0.02384 gram VO_2 = 19.84 per cent.

0.1383 gram gave with $KMnO_4$ 0.06032 gram V_2O_5 = 43.62 per cent.

0.1360 gram gave with $KMnO_4$ 0.05892 gram V_2O_5 = 43.32 per cent.

0.5646 gram gave 0.3035 gram $P_2O_7Mg_2$ = 34.38 per cent. P_2O_5.

0.7186 gram gave 0.3876 gram $P_2O_7Mg_2$ = 34.49 per cent. P_2O_5.

The analyses lead to the formula

$$12P_2O_5 . 12VO_2 . 6V_2O_5 . 5K_2O + 40Aq,$$

which requires:

		Calculated.	Found.	
$12P_2O_5$	1704	34.14	34.38	34.49
$12VO_2$	999	20.02	19.84	19.59
$6V_2O_5$	1096	21.96	22.02	21.72
$5K_2O$	472	9.46	9.11	
$40H_2O$	720	14.42	14.38	
	4991	100.00		

The sum of the three oxides $P_2O_5 + VO_2 + V_2O_5 = 76.12$, as calculated from the formula, and 76.02 as found from the mean of all the analyses. The analyses are very difficult, partly because no perfectly satisfactory method of separating phosphoric oxide from the other oxides has yet been found, and partly because in titrating vanadic dioxide by potassic hypermanganate the end reaction varies with the quantity of phosphoric oxide present. It is true that this variation is usually within narrow limits, but it is sometimes sufficient to affect the result by as much as 0.50 per cent.

The beautiful crystalline green salt which is formed when the black salt above described is dissolved in hot water was also analysed.

0.5918 gram gave 0.3771 gram $PtCl_6K_2$ = 12.37 per cent. K_2O.

0.4766 gram lost with WO_4Na_2 0.0718 gram = 15.06 per cent.

0.1617 gram gave with $KMnO_4$ 0.03405 gram VO_2 = 21.06 per cent.

0.1274 gram gave with $KMnO_4$ 0.02708 gram VO_2 = 21.26 per cent.

0.0840 gram gave with $KMnO_4$ 0.01778 gram VO_2 = 21.16 per cent.

0.1532 gram gave with $KMnO_4$ 0.0659 gram V_2O_5 = 43.01 per cent.

0.1612 gram gave with $KMnO_4$ 0.0689 gram V_2O_5 = 42.77 per cent.

0.1625 gram gave with $KMnO_4$ 0.0699 gram V_2O_5 = 42.99 per cent.

In the determination of the water by fusion with sodic tungstate, the vanadic dioxide is oxidised to pentoxide. Hence it is necessary to add to the percentage of water found — 15.06 — the percentage of oxygen required to convert 21.16 per cent. (mean) of VO_2 to the equivalent quantity of V_2O_5 or 2.03 per cent. This correction was not applied in the case of the first salt described above, because after a rapid fusion the vanadic dioxide appeared not to have been oxidised. In determining the vanadic pentoxide in these salts the oxide is first reduced to VO_2 by boiling with sulphurous acid and then titrated with hypermanganate. From want of material the phosphoric oxide in the green salt was determined by difference only.

The analyses of the green salt correspond with the formula

$$12P_2O_5.14VO_2.6V_2O_5.7K_2O + 52Aq,$$

which requires:

		Calculated.	Mean.				
$12P_2O_5$	1704	30.63	29.65 (diff.)				
$14VO_2$	1166	20.96	21.16	21.06	21.26	21.16	
$6V_2O_5$	1096	19.71	19.73	19.82	19.80	19.58	
$7K_2O$	661	11.88	12.37		12.37		
$52H_2O$	936	16.82	17.09		17.09		
	5563	100.00					

In this class of compounds I found it impossible to determine the sum of the acid-forming oxides by precipitating directly with mercurous nitrate and mercuric oxide. The results of many trials varied within very wide limits. Both the black and green salts are oxidised when heated with nitric acid and evaporated to dryness. Yellow crystalline masses remain, which contain phospho-vana-

dates, and which deserve a careful study as furnishing a new and perhaps better mode of forming that class of salts.

14 : 16 : 6 *Ammonic Phospho-vanadico-vanadate.*—When ammonic metavanadate or divanadate is boiled with a solution of ammonic orthophosphate in large excess, a colorless liquid is formed, which gives, with a solution of vanadic dioxide in chlorhydric acid, after a time, beautiful black or rather intensely deep green crystals, exactly resembling those of the potassic salt already described. The crystals dissolve easily in hot water free from saline matter, but do not crystallise readily from the solution. Of this salt, after careful washing and drying only,

0.7744 gram lost with WO_4Na_2 0.1859 gram = 24.01 per cent. $NH_3 + H_2O$. The oxygen gained by the vanadic dioxide is 2.14 per cent. and 24.01 + 2.14 = 26.15 per cent. $NH_3 + H_2O$.

0.5556 gram gave when heated in a combustion tube 0.1451 gram = 26.11 per cent. $NH_3 + H_2O$.

0.8969 gram gave with $KMnO_4$ 0.2001 gram VO_2 = 22.31 per cent.

0.2018 gram gave with $KMnO_4$ 0.0444 gram VO_2 = 22.19 per cent.

0.5626 gram after reduction with SO_3H_2 gave with $KMnO_4$ 0.2427 gram = 43.13 per cent. V_2O_5.

0.2494 gram after reduction with SO_3H_2 gave with $KMnO_4$ 0.1067 gram = 42.76 per cent. V_2O_5.

0.5325 gram gave 0.0326 gram $(NH_4)_2O$ = 6.13 per cent.

0.5053 gram gave 0.0309 gram $(NH_4)_2O$ = 6.12 per cent.

The mean of the two determinations of VO_2 is 22.25 per cent., and the equivalent in V_2O_5 24.38 per cent., which, subtracted from 42.76 and 43.13 respectively, gives 18.38 and 18.75 for the percentages of V_2O_5.

The analyses correspond closely with the formula

$$14P_2O_5 . 16VO_2 . 6V_2O_5 . 7(NH_4)_2O + 67Aq,$$

which requires :

		Calc'd.	Found.	
$14P_2O_5$	1988	33.21	33.06 (diff.)	
$16VO_2$	1333	22.26	22.31	22.19
$6V_2O_5$	1096	18.30	18.38	18.75
$7(NH_4)_2O$	364	6.08	6.12	6.13
$67H_2O$	1206	20.15	20.01	
	5987	100.00		

A portion of the very dark green salt was boiled with water, and the deep green solution allowed to stand, when much lighter green crystals separated. These were again dissolved and recrystallised. The crystals had a peculiar rusty olive-green surface color. Of this salt,

0.4770 gram gave 0.1013 gram V_2O_5 by $KMnO_4$ = 21.21 per cent., and

0.1014 gram VO_2 = 21.22 per cent.

0.4014 gram gave 0.0249 gram $(NH_4)_2O$ = 6.20 per cent.

0.3062 gram lost with WO_4Na_2 0.0663 gram = 21.65 per cent.

The determination of the sum of the water and ammonia must in this case be corrected for the oxygen required to convert the 21.22 per cent. of vanadic dioxide into vanadic pentoxide, since the ignition was continued with free access of air until the weight of the mass became constant. The correction is of course to be added, so that we have for the total loss 21.65 + 2.03 = 23.68 per cent.

The analyses correspond tolerably well only with the formula

$$10P_2O_5 . 11VO_2 . 5V_2O_5 . 5(NH_4)_2O + 41Aq,$$

which requires:

		Calculated.		Found.	
$10P_2O_5$	1420	33.44		33.89	(diff.)
$11VO_2$	916	21.57	76.50	21.21	76.32
$5V_2O_5$	913	21.49		21.22	
$5(NH_4)_2O$	260	6.12		6.20	
$41H_2O$	738	17.38	23.50	17.48	23.68
	4247	100.00			

As the number of molecules of vanadic dioxide in this salt is uneven, it will be necessary to double the formula in order to obtain a symmetrical structural scheme.

ARSENIO-VANADICO-VANADATES.

The salts of this series are formed with great ease by mixing solutions of alkaline arsenates and vanadates, and adding a solution of vanadic dioxide in excess of chlorhydric acid. On evaporation large very dark green crystals are deposited in abundance. In preparing arsenio-vanadates it is difficult to avoid a partial reduction of the vanadic pentoxide by dust or other organic matter,

and as a rule solutions are obtained which contain both classes of salts. The arsenio-vanadico-vanadates form a very beautiful and well-defined class of salts.

Analytical Methods.—Vanadic dioxide may be determined directly by titration with hypermanganate after addition of sulphuric acid and appropriate dilution. To determine the arsenic present as arsenic pentoxide, the arsenic is first to be brought into the form of arsenous oxide by means of sulphurous acid after adding a little sulphuric acid to the solution. The arsenic may then be precipitated as sulphide by means of sulphydric acid, and weighed on a Gooch filter. The filrate contains all the vanadium in the form of dioxide, which may then be determined by means of hypermanganate. The relation between the two oxides of vanadium is then easily found. The accurate determination of the water of crystallisation in these salts is difficult. They all lose arsenic oxide when heated with sodic tungstate; and the only method which can be safely employed consists in heating weighed portions over a radiating cup of sheet-iron until a constant weight is obtained.

12 : 12 : 6 *Ammonium Salt.*—When ammonic metavanadate or divanadate is boiled with a large excess of ammonic arsenate, a colorless solution is formed. On adding a solution of vanadic dioxide in chlorhydric acid, a dark blue precipitate is formed, which dissolves readily in an excess of dilute chlorhydric acid. No precipitate is formed if the solution of the dioxide contains enough free acid. After standing some hours, a very dark green, almost black, crystalline salt is deposited in quantity. This is to be washed with cold water. The crystals exactly resemble those of the black potassic phospho-vanadico-vanadate already described. They are insoluble in saline solutions, and but slightly soluble in cold water. The solution has a greenish-yellow color. It gives a brick-red indistinctly crystalline precipitate with argentic nitrate, and a dull yellow flocky precipitate with mercurous nitrate. This last becomes crystalline on standing. It will serve to prepare other salts of this series by double decomposition with chlorides. The solution of the salt gives no precipitate with cupric sulphate or baric chloride. In this salt,

1.1623 grams gave with $KMnO_4$ 0.2199 gram $VO_2 = 18.91$ per cent.

0.8719 gram gave with $KMnO_4$ 0.3605 gram $V_2O_4 = 41.37$ per cent.

0.9726 gram gave 0.5500 gram $As_2S_3 = 52.87$ per cent.
0.8246 gram gave 0.4646 gram $As_2S_3 = 52.68$ per cent.
1.0209 gram gave 0.0538 gram $(NH_4)_2O = 5.27$ per cent.

The vanadic pentoxide, after deducting the equivalent of the dioxide found, is 20.65 per cent. The water could not be determined either by heating with sodic tungstate or in a combustion tube, as arsenous oxide sublimed in each case. It is therefore estimated by difference.

The analyses agree fairly well with the formula

$$12As_2O_5.12VO_2.6V_2O_5.5(NH_4)_2O + 7Aq,$$

which requires:

		Calculated.	Found.	
$12As_2O_5$	2760	52.65	52.68	52.87
$12VO_2$	1000	19.08	18.91	
$6V_2O_5$	1096	20.91	20.65	
$5(NH_4)_2O$	260	4.96	5.27	
$7H_2O$	126	2.40	2.40	
	5242	100.00		

It will be observed that this salt may be considered as derived from twelve molecules of an arsenio-vanadate by reduction of one-half the vanadic pentoxide to dioxide and loss of seven molecules of ammonic oxide, since we have

$$12[As_2O_5.V_2O_5.(NH_4)O_2] = 15As_2O_5.12VO_2.6V_2O_5.5(NH_4)_2O + 7(NH_4)_2O + 6O.$$

This relation might be made available in the preparation of the salt. Boiling water instantly decomposes this compound, and gives a deep green solution, which on standing deposits crystals of a peculiar deep olive-green color with a tinge of brown. The black salt corresponds exactly in composition to a phosphorus compound above described, except only as regards water of crystallisation:

$$12P_2O_5.12VO_2.6V_2O_5.5(NH_4)_2O + 7Aq.$$

9:9:8 *Ammonium Salt.*—When boiling water is poured upon the black salt, it instantly becomes deep olive-green upon the surface, and then dissolves to a deep green liquid, which on cooling deposits crystals with a dull olive-green surface color. These may be redissolved and recrystallised a second time. The mother liquor from these crystals has a bright green color, and contains much vanadic acid. In the olive-green salt,

0.4061 gram gave 0.167 gram $(NH_4)_2O$ = 4.12 per cent.

0.2871 gram gave 0.1370 gram As_2S_3 = 44.61 per cent.

0.2871 gram gave 0.1393 gram V_2O_5 by $KMnO_4$ = 48.51 per cent (complete oxidation).

0.1637 gram gave 0.0259 gram VO_2 by $KMnO_4$ = 15.82 per cent.

The analyses correspond tolerably well with the formula

$$9As_2O_5.9VO_2.8V_2O_5.4(NH_4)_2O + 11Aq,$$

which requires:

		Calculated.		Found.	
$9As_2O_5$	2070	44.17	60.17	44.61	60.43
$9VO_2$	750	16.00		15.82	
$8V_2O_5$	1461	31.17		31.17	
$4(NH_4)_2O$	208	4.44		4.12	
$11H_2O$	198	4.22		4.28 (diff.)	
	4687	100.00			

The formula given must be doubled to give a structural scheme in which all the terms will be symmetrically arranged.

It appears at least probable that classes of antimonio-vanadates and antimonio-vanadico-vanadates also exist, but the few experiments which I have been able to make with the small quantity of material at my disposal are not conclusive as to either point, and I hope to be able to return to the subject.

VANADICO-VANADATES.

Salts belonging to this series are formed when solutions of vanadates are mixed with those of vanadic dioxide, and when vanadates undergo partial reduction by the action of any reducing agent. These compounds are often crystalline and well defined. They have, usually at least, a green color.

2:4 *Ammonic Vanadico-vanadate.*—When a solution of vanadic dioxide in chlorhydric acid is added to one of ammonic metavanadate, a fine green crystalline salt separates, but slightly soluble in either cold or hot water. The salt analysed was not recrystallised, but merely washed with cold water and dried upon woollen paper. Of this salt,

1.0470 gram gave 0.0159 gram VO_2 by $KMnO_4$ = 15.21 per cent. VO_2.

1.0470 gram gave 0.0701 gram V_2O_5 by $KMnO_4$ = 66.98 per cent. V_2O_5.

0.1470 gram gave 0.0066 gram $(NH_4)_2O = 4.50$ per cent.
The analyses lead to the formula

$$4V_2O_5.2VO_2.(NH_4)_2O + 8Aq,$$

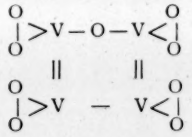
which requires

		Calculated.	Found.
$4V_2O_5$	730.4	66.82	66.98
$2VO_2$	166.6	15.24	15.21
$(NH_4)_2O$	52	4.76	4.50
$8H_2O$	144	13.18	13.31 (diff.)
	1093	100.00	

The following may serve as starting-points for further investigation. When solutions of sodic divanadate and manganous sulphate are mixed and allowed to stand in an open vessel, very dark green well-defined crystals are gradually deposited. There is here, doubtless, reduction from the presence of dust. When a solution of vanadic dioxide in chlorhydric acid is mixed with solutions of the sulphates of zinc, copper, cobalt, or nickel, and of sodic divanadate, dark green crystalline precipitates are formed on standing, which would appear to be vanadico-vanadates, but which, as they are formed in the presence of an excess of a strong acid, may prove to be types of vanadico-vanadic acids. In his valuable paper on the salts formed by vanadic acid, Rammelsberg has described a remarkable compound, which may be regarded as an anhydride of a special form of vanadico-vanadic acid. This compound has the formula

$$V_2O_5 + 2VO_2,$$

and forms black microscopic crystals. Its structural formula may be written:



It is easy to see how acids of various types might be derived from such anhydrides by replacing oxygen by an equivalent of hydroxyl. The existence of very well-defined series of phosphoroso-tungstates and phosphoroso-molybdates, and of similar series

of compounds containing As_2O_3 and Sb_2O_3, would naturally lead to the attempt to form similar classes of complex acids containing V_2O_3. Want of material has prevented me from experimenting in this direction, and I must content myself with directing the attention of other chemists to the subject. Vanadic protoxide appears to possess the properties of a base only, but our knowledge of the subject is so imperfect that it may also be well worth while to determine whether there may not be a class of vanadium compounds corresponding to the hypophospho-tungstates and hypophospho-molybdates.

The existence of classes of phospho-vanadates and arsenio-vanadates embraced under the general formula

$$R_3O_5.V_2O_5.nH_2O$$

would seem to imply that of corresponding chlorides, bromides, etc., of corresponding or analogous types,

$$R'Cl_5.RCl_5,\quad R'Cl_4.RCl_5, \text{ etc.}$$

Various compounds of this kind have already been observed by chemists, though, so far as I am aware, no attempt has been made to classify them or to assign to them their true position as double chlorides, etc., corresponding to double oxides capable of forming complex acids. Examples of this class are the following:

$SnCl_4 + PCl_5$		Casselmann.
$SnCl_4 + POCl_3$		"
$TiCl_4 + POCl_3$		Weber.
$TiCl_4 + PCl_5$		Tüttschew.
$SeCl_4 + SbCl_5$		Weber.
$VOCl_3 + PtCl_4$		Brauner.
$Al_2Cl_6 + 2POCl_3$		Casselmann.
$Fe_2Cl_6 + 2POCl_3$		"
$SbCl_5 + PCl_5$		Weber.
$SbCl_5 + POCl_3$		"

It is at least possible that in these and many similar cases complex or double acids correspond to the double chlorides, and it is probable that the action of such double chlorides upon solutions of acid tungstates and molybdates would produce complex acids containing tungsten or molybdenum and the two acid-forming oxides corresponding to the two united chlorides. I shall

at another time specially consider the compounds of platinous and phosphorous chlorides discovered by Schützenberger.

In my paper upon the vanadium compounds of tungsten and molybdenum I have endeavored to show that many formulas may be reduced to the same types as those of the phospho-tungstates and phospho-molybdates, provided that we assume that a part at least of the vanadic pentoxide is to be regarded as replacing tungstic or molybdic oxide, or that we have the chemical equivalence expressed by the equation

$$m\mathrm{V_2O_3} \cdot \mathrm{O_3} = m\mathrm{WO_3} = m\mathrm{MoO_3}.$$

This hypothesis had the advantage of simplifying many formulas materially, but was wholly unsupported by any positive evidence. I have now shown that there exist classes of phospho-vanadates and arsenio-vanadates which do not contain tungstic or molybdic oxide, but which are exactly parallel to phospho-tungstates, vanadio-tungstates, etc., in composition. Thus we have the salt,

$$12\mathrm{V_2O_5} \cdot \mathrm{P_2O_5} \cdot 3\mathrm{BaO} + 45\mathrm{Aq};$$

and the acid,

$$20\mathrm{V_2O_5} \cdot \mathrm{P_2O_5} \cdot 6\mathrm{H_2O} + 53\mathrm{Aq};$$

corresponding to

$$12\mathrm{WO_3} \cdot \mathrm{P_2O_5} \cdot 3\mathrm{BaO}, \text{ and } 20\mathrm{WO_3} \cdot \mathrm{P_2O_5} \cdot 6\mathrm{H_2O}.$$

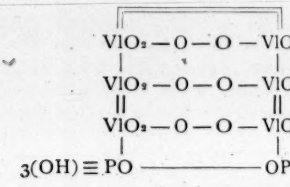
As regards the mode of replacement, however, our views must depend upon the special form of structural formulas which we provisionally adopt. With the view which I have taken of the subject, we may write for a phospho-vanadic acid assumed to have the formula

$$6\mathrm{V_2O_5} \cdot \mathrm{P_2O_5} \cdot 3\mathrm{H_2O},$$

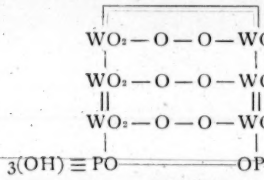
corresponding to the phospho-tungstic acid

$$6\mathrm{WO_3} \cdot \mathrm{P_2O_5} \cdot 3\mathrm{H_2O},$$

the structural formula,

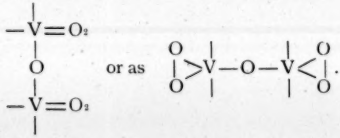


exactly like

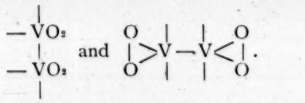


In the formula of the phospho-vanadic acid assumed, I have represented the complex V_2O_2 by VI; and it is easy to see how, structurally, this may be regarded as hexatomic, and as replacing W^{VI} or Mo^{VI}, since we may reasonably suppose that we have

With this view of the subject $(V_2O_2)O_2 = WO_2 = MoO_2$, etc. This mode of formulating compounds containing vanadic pentoxide enables us, as I have shown, to reduce many complex salts to relatively simpler types, and is supported, as we shall presently see, by the formulas of a special class of vanadates exactly corresponding to metatungstates and metamolybdates. On the other hand, in by far the greater number of compounds thus far studied, the complex is to be regarded, I think, as built up of terms of the form RO_2, which may or may not be linked together by one or more atoms of oxygen. In certain cases, therefore, vanadic pentoxide may enter the complex with the structural formula



This last view is strongly supported by the frequent presence of vanadic dioxide, two molecules of which may be considered as associated without a link of oxygen, as in the structural formulas



Finally, as I shall also prove, the structural formula must show what particular modification of phosphoric or vanadic oxide or acid is contained in the salt, since we have not merely ortho-phospho-tungstates but pyro-phospho-tungstates, various modifications of metaphospho-tungstates, and corresponding compounds of molybdenum. It is at least probable that the different modifications of vanadic pentoxide or acid enter in a similar manner. These appear to be very numerous, and a wide field is thus opened for research. I shall return to this subject in the purely theoretical portion of my work.

If the view which I have taken as to the composition of the complex acids containing vanadium be correct, we ought to find some additional support for it in the constitution of the salts of vanadic acid. These have been studied by Roscoe, and especially by Norblad[1] and by Rammelsberg,[2] but the results obtained by these chemists have not been systematised. The very numerous vanadates may be arranged, as I find, under seven groups or series. These are here given for the sake of comparison, typical salts actually obtained in each series being marked by the initials of the analysis. The existence of salts corresponding to other general formulæ is a matter of inference only. As will be seen at once, the first series corresponds to the group of metatungstates, if we compare $V_2O_5.O_4$ with WO_3. Terms 1 and 3 of this series of vanadates have twice the usually given molecular weights.

First Series.

	Vanadates.	Metatungstates.
	$R_2O\ .\ 4V_2O_5$	$R_2O.\ 4WO_3$
R.	$2K_2O\ .\ 6V_2O_5$	$2R_2O.\ 6WO_3$
N.	$3Na_2O.\ 8V_2O_5 + 24Aq$	$3R_2O.\ 8WO_3$
R.	$4Na_2O.10V_2O_5 + 14Aq$	$4R_2O.10WO_3$
	$5R_2O\ .12V_2O_5$	$5R_2O.12WO_3$

Second Series.

N.	$Na_2O.\ V_2O_5$
R.	$2K_2O\ .3V_2O_5$
R.	$3Li_2O\ .5V_2O_5$
	$4R_2O\ .7V_2O_5$

Third Series.

R.	$K_2O\ .2V_2O_5 + 4Aq$
R.	$3Li_2O.4V_2O_5 + 12Aq$
R.	$5Li_2O.6V_2O_5 + 30Aq$
	$7R_2O\ .8V_2O_5$

[1] Bidrag till kännedomen om Vanadiums Amfidsalter. Upsala Universitäts Årsskrift, 1873.
[2] Sitzungsberichte der Königl. Preuss. Akademie der Wissenschaften, 1883, p. 1.

Fourth Series.		Fifth Series.	
R.	$3Li_2O.2V_2O_5 + 15Aq$	R.	$2K_2O.\ V_2O_5 + 3Aq$
	$4R_2O.4V_2O_5$		$3R_2O.3V_2O_5$
	$5R_2O.6V_2O_5$		$4R_2O.5V_2O_5$
	$6R_2O.8V_2O_5$		$5R_2O.7V_2O_5$

Sixth Series.		Seventh Series.	
	$4R_2O.2V_2O_5$	Ro.	$3Na_2O.\ V_2O_5 + 16Aq$
R.	$5K_2O.4V_2O_5 + 7Aq$		$4R_2O.3V_2O_5$
	$6R_2O.6V_2O_5$		$5R_2O.5V_2O_5$
	$7R_2O.8V_2O_5$		$6R_2O.7V_2O_5$

The seven series which I have given embrace, I believe, all known types of vanadates. Each series may be represented by a general formula expressing the relation between the number of molecules of acid and basic oxides. These general formulæ are:

I. $nR_2O.2n + 2.V_2O_5$
III. $nR_2O.\ n + 1.V_2O_5$
II. $nR_2O.2n - 1.V_2O_5$
? $nR_2O.2n - 2.V_2O_5$
V. $nR_2O.2n - 3.V_2O_5$
IV. $nR_2O.2n - 4.V_2O_5$
VII. $nR_2O.2n - 5.V_2O_5$
VI. $nR_2O.2n - 6.V_2O_5$

The arrangement here given makes it probable that at least one series remains to be discovered. Fleitmann and Henneberg have described a phosphate having the formula $6Na_2O.5P_2O_5$. Such a compound would belong to a class of phosphates represented by the general formula—wanting among the vanadates—

$$nR_2O.n - 1.P_2O_5.$$

Roscoe long since established the correspondence of the vanadates and phosphates up to a certain limit. Further investigation is required to show how complete the correspondence is. From an examination of the terms in the seven series of vanadates given above, it will appear that various isomeric modifications are probable among vanadates, and that these correspond, in *form* at least, to the various metaphosphates,—mono, di, tri, tetra, and hexametaphosphates of Fleitmann and Henneberg. These chemists

have also described a class of phosphates corresponding to the first term of the fourth series of vanadates given above. The sodium salt has the formula

$$3Na_2O \cdot 2P_2O_5 + 18Aq.$$

In the imperfect state of our knowledge, all such coincidences are worthy of attention. Another conclusion may perhaps be safely drawn from the systematic arrangement of the vanadates which I have given. This is that meta, pyro, and ortho-vanadates, and the similar compounds of phosphorus, arsenic, antimony, etc., are not *isolated*, but are terms of more complete series. Thus the fifth series embraces the pyro-vanadates and their homologues, while the ortho-vanadates form the first term of the seventh series. In all the series given except the third, the common difference or homologising term is $R_2O \cdot 2V_2O_5$; in the third series, it is $2R_2O \cdot 2V_2O_5$. In some cases only particular terms may exist to represent an entire series, because the special conditions necessary for the stability of other terms may be absent as regards degree. Taking now into account the analogy which I have shown to exist between $V_2O_5 \cdot O_3$ and WO_3 or MoO_3, we may perhaps extend the above conclusions to the cases of the tungstates, molybdates, chromates, etc. Thus we may regard $K_2O \cdot 2CrO_3$ as the initial term of a series corresponding to the third series of vanadates. If we double the usual formula of potassic terchromate, and write it $2K_2O \cdot 6CrO_3$, we shall have the second term in a series corresponding to that of the metatungstates, the first term being the tetrachromate $K_2O \cdot 4CrO_3$.

As a further support to my view that the metatungstates form a homologous series, I shall here describe two new tungstates obtained since the first part of this work was published.

16 : 3 : 4 *Sodio-ammonic Tungstate.*—I obtained this salt accidentally in attempting to prepare a series of glycero-phosphotungstates. The thick syrupy liquid obtained by heating pulverised glacial phosphoric acid with glycerine, and allowing the mixture to stand for some days, was neutralised with ammonia and poured into a hot solution of 12 : 5 sodic tungstate. A beautiful white salt, in shimmering talcose scales, separated as the solution cooled. After careful draining, the salt was recrystallised for analysis. The crystals had a fatty lustre, and were quite easily soluble in hot water. No phosphoric acid could be found in the salt by the most careful testing, and no organic matter. In this salt,

2.3796 grams lost on ignition 0.2825 gram = 11.87 per cent.
2.1691 grams lost on ignition 0.2568 gram = 11.84 per cent.
2.1691 grams gave 1.8209 gram WO_3 = 83.94 per cent.
2.0956 grams gave 0.0973 gram $(NH_4)_2O$ = 4.64 per cent.

The analyses correspond to the formula

$$16WO_3 . 3Na_2O . 4(NH_4)_2O + 18Aq.$$

which requires:

		Calculated.	Found.
$16WO_3$	3712	83.79	83.94
$3Na_2O$	186	4.20	4.21 (diff.)
$4(NH_4)_2O$	208	4.69	4.64
$18H_2O$	324	7.32	7.21
	4430	100.00	

This salt is especially interesting because it supplies a new term to the series of metatungstates—the highest as yet obtained.

12 : 1 : 4 *Sodio-ammonic Tungstate.*—This salt was obtained accidentally in an attempt to prepare a series of ethylo-phosphotungstates. Syrupy phosphoric acid and absolute alcohol were mixed and heated for half an hour to about 80° C., and the mixture allowed to stand twenty-four hours. Ammonia was then added in small quantities at a time until in excess, the liquid being kept cool, the object being to form an ammonic ethylo-phosphate. The solution was then poured into one of 12 : 5 sodic tungstate. After a few minutes an abundant precipitation took place of small shimmering scales, which were drained on the filter-pump, washed with cold water, then dissolved in hot water and filtered. A very small quantity of a very insoluble salt in scales remained undissolved. The filtrate soon gave an abundance of small talcose scales with a fatty lustre.

Of this salt,

1.0293 gram lost on ignition 0.1399 gram = 13.60 per cent.
1.3019 gram lost on ignition 0.1766 gram = 13.57 per cent.
1.0001 gram gave 0.0618 gram $(NH_4)_2O$ = 6.18 per cent.
1.0293 gram gave 0.8689 gram WO_3 = 84.46 per cent.

The analyses correspond to the formula

$$12WO_3.Na_2O.4(NH_4)_2O + 14Aq.$$

which requires:

		Calculated.	Found.
$12WO_3$	2784	84.22	84.46
Na_2O	62	1.87	1.94 (diff.)
$4(NH_4)_2O$	208	6.29	6.18
$14H_2O$	252	7.62	7.42
	3306	100.00	

No trace of phosphoric acid could be detected in the salt, which is perhaps only interesting as furnishing additional evidence of the existence of a class of meta-tungstates in which the ratio of the tungstic oxide to the oxygen of the base is as 12 : 5. In this, as in the 16-atom salt above described, the presence of an excess of free ammonia explains the absence of phosphoric oxide in the compound formed.

My work on the compounds of vanadium is far less complete and thorough than I could have wished, on account of the relatively very high cost of the material. I indulge the hope that what I have done will be found at least substantially correct, and that the whole subject will soon receive the attention of other chemists, who may have a more abundant supply of vanadium salts at their disposal.

(*To be continued.*)

Contributions from the Laboratory of Agricultural and Analytical Chemistry, Cornell University.

II.—MARCHAND DE FECAMP'S METHOD FOR THE DETERMINATION OF FAT IN MILK.

By G. C. Caldwell and S. W. Parr.

While one of us was engaged in 1880 in testing this method for the determination of fat in milk, better known by the name which was given to the special instrument used, Marchand's lactobutyrometer, it was observed that, although the results were in general satisfactory, still there were occasionally differences ranging from 0.2 up to more than 0.4 per cent., between the gravimetric results

and those given by this method.[1] It was further observed that when bran was contained in the ration of the cows producing the milk examined, the difference between the results given by the two methods was in some cases as great as 0.73 per cent.; when the bran was left out of the ration, fairly correct results were obtained again. Since then, other similar unsatisfactory results have been obtained under similar conditions, with differences, in the case of a herd of cows having both bran and malt sprouts in their fodder, of over 1 per cent. between the lactobutyrometric and gravimetric methods. The difference was always a deficiency, and was generally largest with richer milk containing from 4.6 to 4.8 per cent. of fat; but this is not above the limits of the table given by Marchand for reading off the per cent. of fat for the thickness of the ether-fat solution in the lactobutyrometer, nor were the erroneous results always confined to rich milk. The conclusion seems to be unavoidable that the milk is in some way affected by the feed of the cow so as to hinder the solution, in the normal manner, of the fat of the milk by the ether.

Tollens and Schmidt[2] examined this method very carefully, making some improvements in it, and obtained results nearly always within 0.2 per cent. of the gravimetric results, and usually much closer than this. The method as described by them was the one followed in the above-mentioned trials, except that a very little acetic acid was first added to the milk, as prescribed by Marchand, but regarded as unnecessary by them; much better results were obtained in this laboratory with it than without it.

Unsatisfactory results have been reported also by others besides ourselves.[3] Liebermann, while allowing, as most of the other authors referred to also do, that good results are usually obtained, suggests that his poor results may be due to some quality of the milk dependent on the age of the cow; we have tested this suggestion, but could not confirm it.

Vieth,[4] chemist of the Aylesbury Dairy Company (English), has tested the method by comparing the results obtained on 1439 samples of milk with gravimetric results; he concludes that with milk containing from 3.0 to 3.6 per cent. of fat the results are satis-

[1] First Report, Cornell University Experiment Station, 1880, 59.

[2] Journal für Landwirtschaft, 1878, 361; 1879, 145.

[3] Thoenor: Repertorium der analytischen Chem. **4**, 100. Skalweit: *Ibid.* **4**, 132. Labesius: Milch Zeitung **13**, 760. Liebermann: Fres. Zeitschrift **23**, 485.

[4] Forschungen auf dem Gebiete der Viehhaltung, 1885, 2d series, 349.

factory, but that with poorer or richer milk they are not; the results with the former being sometimes as much as 1 per cent. and often 0.5 to 0.6 too high, and with the latter sometimes 0.4 per cent. too low. But while mentioning the poverty or richness of the milk in fat as one of the conditions affecting the results of its determination by the lactobutyrometer, he acknowledges that other conditions also affect the working of the process, and among these he mentions briefly the feed of the cow.

Others commend the method without qualification. Dietzsch,[1] chemist of the Anglo-Swiss Condensed Milk Company, states that of from fifty to a hundred determinations of fat made every day in his laboratory by this method, many are controlled by gravimetric methods, and that the results by the two methods always agree within 0.1 per cent. H. von Peter[2] affirms that the method gives good results, even in unskilled hands. In Weimar[3] the method is recognised before the courts as legal. Schmoeger,[4] of the dairy experiment station at Proskau, gets good results, although generally 0.2 per cent. too low. Schulze and Krämer[5] consider the method to be as good as any for the quick determination of fat in milk, but they imply that something better is desirable.

The great practical value of so simple a method as this one under consideration for the determination of fat in milk, is not to be questioned; and its usefulness to the dairyman or the milk inspector becomes very much enhanced by combination with Fleischman and Morgen's formula for calculating the per cent. of total solids, from the two known data, the specific gravity and the per cent. of fat;[6] thus everything that needs to be known about a sample of milk for practical purposes can be learned with sufficient accuracy in a very short time, and without the use of a balance, the specific gravity being determined by a delicate areometer. But in order that the method shall possess this value it is essential that it shall not be liable, under certain conditions of which the analyst might be in most cases quite ignorant, to such serious error as we have shown it to be in our own experience and that of others; and it is most desirable, to say the least, that it should not be necessary, as is generally acknowledged by most of those who have tested the method, that even under ordinary conditions a possible error of

[1] Repertorium der analytischen Chemie **4**, 132.
[2] Journal für Landwirtschaft **32**, 197.
[3] Milch Zeitung **9**, 618.
[4] Journal für Landw. **29**, 129.
[5] Milch Zeitung **4**, 1415.
[6] Journal für Landwirtschaft **33**, 251.

0.2 to 0.3 must be granted, or from 7 to 8 per cent. of the total fat in average milk.

We offer the following contribution towards securing a greater degree of reliability in the use of the lactobutyrometer. Although we have not attained full success, we seem, so far as our results go, to have at least obviated the liability to error on account of the character of the ration on which the milk is produced.

The most important requisite for success is precise attention to the character of the reagents used. In the first place, Marchand directed that a few drops of sodium hydrate be first added to the milk. Schmidt and Tollens concluded that such addition was unnecessary, and omitted it in their directions; others, however,[1] hold that it is better to use this reagent. We have found it to be quite essential, at least in the examination of the milk of cows having bran or some other kinds of concentrated fodder in their ration; and we have observed that, even when its addition is not necessary for this reason, still it is useful; when used in sufficient quantity it prevents the formation of the abundant precipitate of casein that appears, in its absence, in consequence of the addition of the alcohol and the acetic acid, and in which some of the fat solution is liable to become entangled instead of continuing its course to the surface. Moreover, it appeared on microscopic examination of the milk that in the case of different samples the fat globules were unequally attacked by the ether when no alkali was used, and that this inequality disappeared in the presence of alkali; in such presence solution of the fat takes place much more easily. Ammonia was found to answer this purpose as well as any other alkali, and at the same time there is less danger of any saponification of the fat, than if sodium or potassium hydrate or carbonate is used,[2] although, even with fixed alkali, no saponification could be detected in several careful trials. If, however, more than a very little fixed alkali is used, apparently a gelatinous albuminate is formed, which causes as much trouble as the precipitated casein, in entangling the ether-fat solution; with ammonia no such difficulty appears.

In the second place, although Tollens and Schmidt mention the importance of maintaining certain relative proportions of alcohol and ether, our experience has shown that even more careful atten-

[1] Schulze and Krämer, *l. c.* H. von Peter, *l. c.* Vieth, Milch Zeitung **12**, 261. Adam, Comptes Rendus **87**, 290. Schmoeger, *l. c.*

[2] Christian. Technology of Soap and Candles, 74.

tion to this matter is necessary than they appear to require, for account must be taken of the alcohol in the ether itself, which in the case of ordinary ether is a variable quantity. It appears that, alkali being used as above mentioned, by maintaining an exact relation between the proportions of pure ether, alcohol, and water (of the milk), all of the fat and a portion of the ether will form together a very nearly definite mixture in the proportion of one part of the former to four of the latter; this mixture rises to the surface and constitutes the layer of ether-fat solution which is measured in the lactobutyrometer; but Marchand and others who have given directions for the process allow that a certain constant quantity of the fat remains in the liquid on which the ether-fat solution floats.

Absolute alcohol being miscible with both water and ether in all proportions, it is possible with a given quantity of ether and water to secure a complete mixture of these two unmiscible liquids, by the use of a certain quantity of alcohol. If with such a mixture a known quantity of pure butter fat be mixed, it can all be obtained again by careful, complete removal of the ethereal solution that collects at the surface, expelling the ether and drying and weighing the residue. This was proved by repeated trials. If for the quantity of water given milk be substituted, the ether-fat solution rising to the surface will consist of ether and fat only, and will contain all the fat of the milk, as was also proved by drawing off this solution and estimating the fat in it by weight. In fact, as has been proposed by Adam,[1] a method is hereby indicated, quicker than any yet given, for the gravimetric determination of fat in milk, the reliability of which we propose to test further.

The proper proportions of ether, alcohol and water (of the milk) necessary to secure the conveyance of all of the fat of the milk to the surface of the mixture in the form of an ether-fat solution containing very nearly one part of fat to four of ether, we have found by numerous trials to be 75 parts of pure ether, 100 of absolute alcohol and 135 of water. These proportions may be secured by mixing together 8 parts of Squibb's stronger ether, which contains 6 per cent. of 85 per cent. alcohol, 12 parts of 80 per cent. alcohol and 11 parts of water.

The following method of conducting the determination of the fat in milk with the lactobutyrometer, worked out in accordance

[1] Comptes Rendus **97**, 290.

with these principles, is proposed as a substitute for the method given by Schmidt and Tollens, which is, we believe, the one most generally followed.

The form of the instrument that we have used is represented in the adjoining figure. It is made of moderately thick-walled tubing (about 1 mm.); the stem is about 23 cm. and the bulb about 8 cm. long. It is important that the shoulder between the stem and the bulb should not be too abrupt. The bore of the stem is about 6 mm. and it is graduated in $\frac{1}{20}$ cc. The wider part of the tube has such a capacity that in passing from the lowest graduation on the stem to the inner end of the stopper in the lower mouth, one passes from 5 to 33 cc.; then the ether-fat solution will always come within the range of the graduation on the stem. This instrument differs from that originally given by Marchand, only in being open at the bottom as well as at the top; this is a matter of some importance with reference to cleaning and drying it. The narrow stem in which the ether-fat solution collects makes more accurate readings possible than is the case with the wider tube with the same width of bore throughout, such as is now commonly used. These butyrometers were made for us by Emil Greiner, of New York.

Closing the lower mouth with a good cork, 10 cc. of the well mixed sample of milk are delivered into the well dried tube from a pipette, then 8 cc. of ether (Squibb's stronger) and 2 cc. of 80 per cent. alcohol. Close the smaller mouth of the tube with a cork, and mix the liquids by thorough shaking, which, however, need not be either violent or prolonged. Both corks should be held in place by the fingers during this operation, and the upper one should be once or twice carefully removed to relieve the pressure within, otherwise it is liable to be forced out suddenly unless carefully watched, with consequent danger of loss of material. Lay the tube on its side for a few minutes and then shake it again; add 1 cc. of ordinary ammonia diluted with about its volume of water, and mix as before by shaking; then add 10 cc. of 80 per cent. alcohol, and mix again thoroughly by moderate shaking, and holding the tube from time to time in an inverted position while the lighter portion of the liquid rises to the surface.

Now put the tube in water kept at 40° to 45°, till the ether-fat solution separates; this separation may be hastened by transferring the tube to cold water after it has stood in the warm water for a few minutes, and then returning it to the warm water. Finally transfer the tube to water kept at about 20° C., and as the level of the liquid falls in the stem by the contraction of the main body of it in the bulb, gently tap the side of the tube below the ether-fat solution, to dislodge any flakes of solid matter that may adhere to the walls; then as this solution finally takes its permanent position in the tube, its volume will not be increased by the presence of such foreign matters. The readings are to be taken from the lowest part of the surface meniscus to the line of separation between the ether-fat solution and the liquid below it.

The following table gives the percentages of fat corresponding to each tenth of a cubic centimetre of ether-fat solution down to 1 cc. and for each twentieth of a cubic centimetre thereafter.

Reading.	Per cent. of fat.	Reading.	Per cent. of fat.
3	1	13.5	3.51
4	1.23	14.0	3.63
5	1.47	14.5	3.75
6	1.71	15.0	3.87
7	1.95	15.5	4.00
8	2.19	16.0	4.13
9	2.43	16.5	4.26
10	2.67	17.0	4.39
10.5	2.79	17.5	4.52
11.0	2.91	18.0	4.65
11.5	3.03	18.5	4.78
12.0	3.15	19.0	5.01
12.5	3.27	19.5	5.14
13.0	3.39	20.0	5.27

This butyrometric method has been applied with fairly satisfactory results to the milk of a herd of cows receiving bran and cotton-seed meal in their ration. Equally good results have been obtained, usually with the milk of a single cow, whether having bran in her food or not, and with rich milk of Jersey cows. Of these results we give here only the last, when, at the same time, Soxhlet's well-known areometric method was taken into the comparison. In these tests the gravimetric determinations were made

by one of us by the convenient method devised by Dr. S. M. Babcock.[1] The milk is dried down on asbestos in a large test tube, with a small hole blown out at the bottom so that a current of air can be forced through it while in the drying bath. The quantity of asbestos taken is large enough to absorb 5 cc. of milk without dripping. The tube with its contents is then treated with ether in the usual manner in a fat extractor of the special form in use in this laboratory for several years.[2] The determinations by the butyrometer were made by one of the instructors in the laboratory who had not used the instrument before, and those by Soxhlet's method by another instructor. The results, including the duplicates, are given in the following table:

		Gravimetric.	Butyrometer.	Soxhlet.
I. Milk of the herd of cows.	1	3.660	3.59	3.57
	2	3.657	3.57	3.59
II. " " "	1	3.536	3.54	3.46
	2	3.539	3.52	3.41
III. Milk of cow having bran in her ration.	1	2.793	3.11	
	2	2.791	2.99	
IV. Milk of the herd.	1	3.305	3.31	3.23
	2	3.305	3.35	3.18
V. Milk of another cow having bran in the ration.	1	2.992	2.97	2.93
	2	2.992	2.99	2.96
VI. Milk of the same cow, another day.	1	3.053	3.38	2.98
	2		3.32	3.01

These results show that Marchand's butyrometric method as conducted by us is capable of a degree of accuracy that leaves nothing to be desired, and that in this respect it is not at all inferior to Soxhlet's method, while it is very much more simple, and can much more safely be put into unskilled hands. But, while so much can be claimed for it when applied to the mixed milk of a herd of several cows, more or less serious departures from such close agreement with the gravimetric results sometimes appear when the milk of a single cow is analysed, as shown in III; but in this case, while the butyrometer gave tolerable results, Soxhlet's method failed entirely; even after standing five hours, the layer of ether-fat solution in the mixing bottle, which should be over two centimetres thick, was hardly a millimetre thick. Of course no

[1] Second Report of the New York State Experiment Station, 1883, 169. [2] *Ibid.* 1880, 25.

reading could be taken of the specific gravity of this solution. This is not the first time that such a singular anomaly has been observed in working with this method. When the milk of another cow from the herd, having the same ration as III, was taken, while we obtained on one day excellent results by both the volumetric and the areometric methods, on the next day the volumetric method failed again to give perfect satisfaction.

Reserving further discussion of the subject till after the completion of the investigations, which are to be continued in this laboratory during the coming season, we will for the present simply say that we appear to have succeeded in so improving the method of analysis under consideration that at least useful results can be obtained under conditions of feeding of the cows, which before, in some way, caused the results to be utterly unreliable.

III. — A TEST OF CERTAIN METHODS FOR THE ESTIMATION OF THE SEVERAL ALBUMINOIDS IN COW'S MILK, AND OF THE INFLUENCE OF THE FOOD ON THE RELATIVE PROPORTIONS OF THESE ALBUMINOIDS.

By S. W. Parr.

The primary object of this investigation was to discover if possible the cause of certain difficulties encountered in this laboratory in the use of Marchand's lactobutyrometric method for the determination of fat in milk. It was undertaken at the suggestion of Prof. G. C. Caldwell and carried out under his supervision. A partial solution of the difficulties mentioned was reached from a somewhat different direction; but the results of these experiments may possess some value for the information that they furnish in regard to the two points mentioned in the title of this paper.

The milk analysed was taken from a cow of common breed, about six years of age and six weeks in lactation. Three series of analyses were made, with reference to the albuminoids only, corresponding to three different rations, one of which contained no concentrated fodder. Each sample was analysed in duplicate, and also according to two different methods: first, for the total albuminoids by Ritthausen's method, of which a full description has

recently been given by Prof. Leeds in a paper on Woman's Milk;[1] second, for three forms of albuminoids in milk according to Pfeffer's method.[2]

In both methods dried and weighed filters were necessarily used; but by weighing the filters in short, large test-tubes, one of which had the rim cut off, and was just small enough to slide into the other, accurate results were obtained.

In the first method, for total albuminoids, as described by Prof. Leeds, the precipitation is accomplished by means of copper sulphate. The directions are to dry this precipitate "to a certain point," and pulverise before extracting the fat with ether. This point was found to be best attained by allowing the precipitate to drain thoroughly, or by drying it at a low temperature so that a crust shall not be formed on it. When in this cheesy form it was finely cut with a spatula and dried at 100° C.; then if double filters were used, by properly folding them so as to securely enclose the precipitate, it could be still further pulverised by pounding with a pestle upon a smooth surface.

The method for the estimation of the three different albuminoids need not be repeated here in full. The casein is precipitated by hydrochloric or acetic acid, the albumen by boiling, and the "third albuminoid" by tannic acid. The results of a number of analyses by these methods under the varying conditions of feed are given in the following table.

	Ration. Hay, Indian meal and Bran.		Ration. Hay.		Ration. Hay, Indian meal, Cotton-seed meal, Bran.	
Casein.	2.998	2.658	2.688	2.718	2.946	2.949
	2.500	2.558	2.748	2.706	...	2.819
	2.550	2.781	2.452	2.379	3.140	2.960
	...	...	2.564	2.555	3.220	3.200
Average.	2.683	2.666	2.613	2.589	3.102	2.982
Albumen.	.455	.462	.375	.300	.400	.423
	.445	.480	.384	.395	.415	.528
	.443	.445	.384	.288	.456	.509
	...	...	.223	.284	.466	.460
Average.	.447	.462	.341	.317	.434	.480

[1] Chemical News **50**, 263. [2] Fresenius, Zeitschrift für analyt. Chemie **22**, 14.

	Ration. Hay, Indian meal and Bran.		Ration. Hay.		Ration. Hay, Indian meal, Cotton-seed meal, Bran.	
3d albuminoid + tannin.	.392	.417	.246	.208	.280	.285
	.266	.262	.270	.288	.370	.372
	.252	.290	.280	.288	.269	.249
	...	...	.315	.315	.330	.348
Average.	.303	.323	.278	.275	.312	.313
Sum.	3.433	3.451	3.232	3.181	3.848	3.775
Total albuminoids (Ritthausen's method).	3.218	3.178	2.912	2.854	3.378	3.497
	2.925	2.945	2.705	2.654	3.451	3.408
	2.988	3.045	2.778	2.838	3.403	3.434
	3.193	3.205	3.065	3.043	3.273	3.163
Average.	3.081	3.093	2.865	2.847	3.376	3.375

With regard to these results it may be noted that for the total albuminoids, as determined by Ritthausen's method, the agreement between duplicates is very satisfactory; between different samples it is as close as could be expected, when it is considered how much the milk of the same cow may vary in composition from day to day. In the case of the sum of the three albuminoids determined separately the agreement is also close; but these total quantities exceed those obtained by Ritthausen's method by from 0.35 to 0.47 per cent., or a quantity closely approaching the percentages found of Pfeffer's third albuminoid.

The only evident source of error in these determinations of the separated albuminoids is one of excess; for this third albuminoid is weighed in the form of a precipitate containing an unknown quantity of tannin with the albuminous substance. On the other hand, it cannot be affirmed that the results obtained for the total albuminoids by Ritthausen's method are too low, for the reasons that the only evident source of error in this case would be the deduction of too large an amount of ash from the weight obtained of albuminoids plus non-volatile matter, owing to the uncertain and different combinations of the copper in the precipitate weighed and in the ash. The weight of ash deducted was 0.0727 gram; of this 0.061 gram was metallic copper, as calculated from the quantity of copper salt used in the precipitation. If to this last weight we add the actual casein ash found by analysis when no metallic base had been added, or 0.0112 gram, we have as the

sum 0.0722, which corresponds closely with the above deduction actually made. In burning the precipitated albuminoids with the filter-paper the copper is largely reduced to the metallic condition; in the precipitate it undoubtedly exists as a copper albuminate. It would appear from these considerations that we may fairly conclude that the method employed for the determination of the total albuminoids gives nearly, if not quite, correct results.

This throws upon the other method, in which the albuminoids are determined separately, the responsibility for the want of agreement between the two methods in the total results; at least a part of the error is due, as has been shown, to the method of estimating the residue of albuminous matter that is neither casein nor albumen.

Whether this method is accurate enough or not for the purpose of comparing different samples of milk produced under different conditions, must be decided by further experience; but it will be seen in the table, that while there is a marked difference, and always in the same direction, in the proportion of albumen, between the milk produced on hay alone, and that produced on the richer ration that preceded or followed it, which holds good for each sample, as well as for the averages of all the samples analysed on each ration, there is no such constant difference in respect to the "third albuminoid," although such a difference does appear, to a slight extent, in the averages of the results for this albuminoid; this notable difference appears also in the total albuminoids, by either method of determination, especially in passing from the hay to the following ration of hay and rich nitrogenous foods.

IV.—SOME NEW QUALITATIVE METHODS.

By Fred. A. Holton.

The Separation of Iodine and Bromine.—This separation is based on the fact that an alkaline iodide liberates free iodine in presence of potassium chromate and dilute nitric acid, while the bromide is not thus decomposed.

$$6NaI + 2K_2CrO_4 + 16HNO_3 = Cr_2(NO_3)_6 + 6NaNO_3 + 4KNO_3 + 8H_2O + 6I.$$

The operation is as follows: About 0.5 gram of the substance is boiled in 15 cc. of a saturated solution of sodium carbonate for a few minutes, and filtered. To 1 cc. of this solution containing the

iodine in the form of sodium iodide, dilute nitric acid (sp. gr. 1.156) is added in slight excess, then 2 or 3 drops of potassium chromate (8 of salt to 100 of water), and 1 cc. of carbon disulphide, and the whole is shaken thoroughly. The iodine is taken up by the carbon disulphide, and is removed by filtering through a moistened filter. To the filtrate 1 cc. of moderately strong chlorine water is added, and then ½ cc. of carbon disulphide. After shaking, the brown color of bromine appears.

Too much potassium chromate is to be avoided, on account of the yellow color it imparts to the solution in which bromine is to be detected. This, however, may be obviated by diluting with water after shaking the last time.

Test for Chromic Acid.—This reaction between an iodide and a chromate, in the presence of free acid, serves as an extremely sensitive test for chromic acid. The solution to be tested having been boiled with sodium carbonate as above, to transpose the chromate, 1 cc. of this solution is slightly acidified with dilute hydrochloric acid (about 1.025 sp. gr.), and 1 or 2 drops of pure potassium iodide (1–10), and 0.5 cc. of carbon disulphide are added. A violet color appearing in the disulphide indicates chromic acid.

Arseniates, antimoniates, stannates, ferricyanides and chlorates also liberate iodine from the iodide under the above conditions. The interference of these acids may be obviated in the following manner: The sodium carbonate solution is made acid with acetic acid, a little barium chloride is added, the precipitate washed thoroughly, and then a little dilute hydrochloric acid is poured over the precipitate. The filtrate is now tested with potassium iodide and carbon disulphide as above.

To apply this test for *chromium*, in the precipitate of the hydrates of third and fourth group metals by barium carbonate, as obtained in the systematic course for analysis by Fresenius,[1] this precipitate is carefully washed free of nitrates by repeated decantation with hot water, a small portion of the residue is fused with pure sodium carbonate, boiled with a little water, filtered, the filtrate acidified with dilute hydrochloric acid, and brought nearly to boiling, two or three drops of oxalic acid are added to decompose any permanganate present, the solution is cooled completely, and tested with a drop or two of potassium iodide and 0.5 cc. carbon disulphide.

ITHACA, N. Y., *September*, 1885.

[1] Fresenius. Qualitative Analysis, Edition 1880, 295.

BENZOYLACETIC ACID AND SOME OF ITS DERIVATIVES.[1]

PART II.

BY W. H. PERKIN, Jun., Ph.D., *Privatdocent at the University of Munich.*

In Part I of this research I described the preparation and properties of ethylic benzoylacetate and of benzoylacetic acid, as well as of some compounds in which the hydrogen-atoms of the methylene group of the former are displaced by alcoholic radicles, such as ethyl-, diethyl-, and allyl-benzoylacetic ether, together with the products of their hydrolysis. Before describing the more complicated reactions in which ethylic benzoylacetate takes part, I should like to give the results of the experiments I have made with some of these compounds since the publication of Part I.

It has been found that although the substituted etheric salts of the benzoylacetic acids cannot be distilled without decomposition under the ordinary pressure, they can easily be obtained pure by distillation under diminished pressure. Using an apparatus similar to that described by Thorne, I have succeeded in purifying the monethyl- and allyl-derivatives described in the previous paper. If the crude product of the action of ethyl iodide on ethylic benzoylacetate is distilled under a pressure of 225 mm., a small quantity of acetophenone passes over first, and then the temperature rises rapidly to 220°, between which and 240° nearly the whole comes over as an almost colorless oil, leaving but a small residue. On repeatedly refractioning this oil under the same pressure, it distils mostly between 230–235°. The portion used for analysis boiled at 231–232° at 225 mm.

0.1550 gram substance gave 0.1020 gram H_2O and 0.4016 gram CO_2.

	Found.	Theory. $C_6H_5.CO.CH(C_2H_5).COOC_2H_5$.
C	70.66 per cent.	70.91 per cent.
H	7.31	7.27
O	22.03	21.82

Ethylic ethylbenzoylacetate is a colorless, strongly refracting oil possessing an aromatic odor and burning taste. When pure, it

[1] Communicated by the Author.

appears to distil at the ordinary pressure almost without decomposition. The boiling points of the pure substance were incidentally noticed as being

210—211°	at 90 mm.
223—224	150
231—232	225

Ethylic ethylbenzoylacetate is insoluble in potassic hydroxide solution, but appears to give a sodium compound on mixing it with sodic ethoxide. On continued boiling, no condensation-product is formed corresponding with the dehydrobenzoylacetic acid, which is so easily obtained by heating ethylic benzoylacetate for a short time by itself. This reaction I hope to describe in Part III of this paper. Ethylic acetoacetate and ethylacetoacetate behave in a precisely similar way. On passing ethylic acetoacetate through a tube at a dull red heat, it is almost completely decomposed, yielding as much as 20 per cent. of its condensation-product, dehydracetic acid, whereas ethylic ethylacetoacetate passes through almost unaltered, no trace of the analogous acid being formed.

Ethylic allylbenzoylacetate may also be purified in exactly the same way as ethylic ethylbenzoylacetate. On submitting the crude product of the action of allyl iodide on ethylic benzoylsodacetate to distillation under a pressure of 225 mm., nearly the whole passes over between 225–245° as a peculiar greenish-colored oil, with a slight reddish fluorescence. This coloration can only be removed by repeated fractioning, and even then it often returns on standing.

Pure ethylic allylbenzoylacetate boils at

220°	under 100 mm. pressure.
226—227°	130
240—241	225

As it is difficult to burn, it is necessary that the combustion should be done with chromate of lead. The following numbers were obtained:

0.1491 gram substance gave 0.0902 gram H_2O and 0.3924 gram CO_2.

	Found.	Theory. $C_6H_5.CO.CH(CH_2.CH:CH_2).COOC_2H_5$.
C	71.77 per cent.	72.41 per cent.
H	6.72	6.89
O	21.51	20.69

Ethylic allylbenzoylacetate possesses the peculiar disagreeable odor characteristic of most allyl compounds. It does not solidify at 0°. The solution in acetic acid takes up bromine readily, especially if warmed, and without evolution of hydrobromic acid.

Ethylic benzoylacetate itself cannot be purified by distillation under diminished pressure, the greater part being decomposed, owing to the comparative slowness with which distillation takes place. When distilled as rapidly as possible (at 200 mm.) a portion passes over between 220–225°, consisting of nearly pure ethylic benzoylacetate, but a large residue is left containing considerable quantities of dehydrobenzoylacetic acid.

Having obtained ethylic monethyl- and allyl-benzoylacetates in a pure state, it was next thought necessary to repeat the hydrolysis with potash, in order, if possible, to obtain the acids in a pure state, but even when very dilute alcoholic potash was used, the acids were always mixed with benzoic acid, in some cases to a very considerable extent.

It was then thought that hydrolysis with sulphuric acid might give better results, and several experiments were therefore tried, using ethylic benzoylacetate itself in the first case.

On mixing ethylic benzoylacetate with twenty times its volume of concentrated sulphuric acid, and allowing it to remain for some time, the mixture becomes thick and dark-colored, small quantities of carbonic anhydride and sulphurous anhydride being given off.

After standing for fourteen days, the product was poured into ice water; this caused the precipitation of a thick dark brownish oil, which partly solidified on prolonged agitation. This uninviting body was separated from the aqueous solution by filtration, washed well with water, and then spread out on a porous plate; in this way the dark brown oil was almost completely removed from the crystals in two or three days, leaving them as a hard yellowish crystalline crust. After recrystallising it several times from warm benzene, the substance was easily obtained pure, melting between 103–104°, and presenting all the appearance of benzoylacetic acid.

On adding a drop of ferric chloride to the alcoholic solution, it gave the beautiful violet coloration mentioned in Part I, and the acid itself on dry distillation split up quantitatively into carbonic anhydride and acetophenone. There can be no doubt, therefore, that the substance was pure benzoylacetic acid. Experiments were next tried to ascertain if ethylic ethylbenzoylacetate could also be

hydrolysed in the same way. A small quantity of this ethereal salt was mixed with nearly three times its volume of concentrated sulphuric acid, and allowed to remain for three weeks. The solution became brownish-colored, but not nearly so dark as in the case of ethylic benzoylacetate itself; on adding water, an almost colorless oil was precipitated, which was removed by shaking with ether, and on evaporating the ether, a yellowish oil remained behind; this when exposed over sulphuric acid in a vacuum deposited crystals, apparently ethylbenzoylacetic acid. The quantity, however, was unfortunately too small for analysis, so that it will be necessary to repeat the experiment with more material before I can be certain that this method is of general application for the hydrolysis of ethylic benzoylacetate derivatives.

Part II of this research comprises the preparation and properties of ethylic nitrosobenzoylacetate, dibenzoylacetic acid, di- and tribenzoylmethane, the reduction of ethylic benzoylacetate, the action of phosphorous pentachloride on ethylic benzoylacetate, and the condensation of the latter with benzaldehyde.

Ethylic Benzoylnitrosoacetate.

By the action of nitrous acid on ethylic acetoacetate, Victor Meyer obtained ethylic nitrosoacetoacetate, according to the equation,

$$CH_3.CO.CH_2.COOC_2H_5 + NOOH = CH_3.CO.C(N.OH).COOC_2H_5 + H_2O.$$

After a series of admirable researches, he proved that the formula of this compound was not $CH_3.CO.CH(NO).COOC_2H_5$, and therefore did not contain the nitroso-group NO, as was at first supposed, but that it was in reality an isonitroso-body, having the constitution $CH_3.CO.C(N.OH).COOC_2H_5$, and containing the isonitroso-radicle: N.OH.

With the exception of ethylic malonate, ethylic acetoacetate is the only compound which is capable of being converted into an isonitroso-derivative; for the substituted acetoacetates, such as ethylic ethylacetoacetate, $CH_3.CO.CH(C_2H_5).COOC_2H_5$, possessing only one hydrogen-atom which is capable of being substituted by any group, cannot combine with the dyad radicle NOH.

The nitroso-derivative of the whole molecule is therefore never formed by the action of nitrous acid on such bodies, but the

ethereal salt being first hydrolysed, carbonic anhydride is given off, and the nitroso-ketone remains behind:

$$\underset{\text{Ethylic ethylacetoacetate.}}{CH_3.CO.CH(C_2H_5).COOC_2H_5} + NOOH =$$

$$\underset{\text{Nitrosoethylacetone.}}{CH_3.CO.C(C_2H_5):NOH} + C_2H_5OH + CO_2.$$

It therefore appeared interesting to try the action of nitrous acid on ethylic benzoylacetate and some of its derivatives, in order to determine whether they would follow the same law or not.

After several trials, the following was found to be the best method of preparing ethylic nitrosobenzoylacetate:

Ethylic benzoylacetate is first dissolved in dilute sodic hydroxide solution, filtered, mixed with an excess of sodic nitrite, and cooled down below 0° in a freezing mixture. Dilute sulphuric acid is then slowly added from a burette until the mixture is decidedly acid, care being taken that the liquid does not get warm. After a short time, more sodic hydroxide solution is added; this dissolves all that was precipitated by the sulphuric acid, producing an intense yellow solution, a sign that a nitroso-body has been formed. Last of all, the ethylic nitrosobenzoylacetate is precipitated by adding an excess of sulphuric acid. It separates as an oil, which, however, on agitating soon solidifies to long colorless needles. These are collected, well washed with water, and separated from any oily matter by spreading them out on a porous plate. In order to purify it, it is dissolved in a little hot alcohol, and water added until it becomes milky. The whole is then warmed up again and allowed to stand, when pure ethylic nitrosobenzoylacetate separates out in beautiful long colorless needles; on analysis, these gave the following numbers:

I. 0.1711 gram substance gave 0.0813 gram H_2O and 0.3729 gram CO_2.

II. 0.1566 gram substance gave 0.0730 gram H_2O and 0.3423 gram CO_2.

I. 0.2617 gram substance gave 16 cc. N, bar. = 718 mm., $t.$ = 21°.

II. 0.2154 gram substance gave 12.5 cc. N, bar. = 716 mm., $t.$ = 18°.

	Found.		Theory.
	I.	II.	$C_{11}H_{11}NO_4$.
C	59.44	59.62 per cent.	59.73 per cent.
H	5.28	5.18	4.97
N	6.56	6.31	6.33
O	28 72	28.89	28.96

From its analogy to ethylic nitrosoacetoacetate, this compound must have the formula $C_6H_5.CO.C(N.OH).COOC_2H_5$.

Ethylic nitrosobenzoylacetate melts at 120–121°. It is easily soluble in alcohol, ether, benzene, and chloroform, sparingly in water. It dissolves easily in alkalis, forming a yellow solution like all nitroso-bodies, and on acidifying is reprecipitated unchanged. It is decomposed by dry distillation with separation of charcoal and formation of hydrocyanic acid. A heavy oil passes over, which soon solidifies, and then melts at 110–114°; it is perhaps impure benzoic acid.

On treating ethylic nitrosoacetoacetate with alkalis, it is decomposed in the same way as ethylic acetoacetate itself, yielding nitrosoacetone instead of acetone. It was thought likely, therefore, that ethylic nitrosobenzoylacetate under the same conditions would give nitrosoacetophenone.

In order to test this, 3 grams of ethylic nitrosobenzoylacetate were dissolved in dilute potash, and allowed to remain for some days at the ordinary temperature, when the yellow solution of the nitroso-derivative became quite colorless. The product was then cooled in a freezing mixture, acidified with sulphuric acid, and extracted with ether. On evaporating the ethereal solution, it deposited a colorless crystalline substance, which contained but traces of nitrogen, and therefore could not be nitrosoacetophenone. It is easily soluble in warm water, and on cooling crystallises in small thick prisms, which were collected, dried over sulphuric acid in a vacuum, and analysed, with the following results:

I. 0.1797 gram substance gave 0.0684 gram H_2O and 0.3962 gram CO_2.

II. 0.1247 gram substance gave 0.0477 gram H_2O and 0.2747 gram CO_2.

	Found.		Theory.
	I.	II.	$C_9H_8O_4$.
C	60.13	60.08 per cent.	60.00 per cent.
H	4.22	4.25	4.44
O	35.65	35.67	35.55

The compound therefore appears to have the formula $C_9H_8O_4$. It crystallises from water in small prisms melting at 125°. It dissolves easily in alkalis, forming a colorless solution. On precipitating the neutral solution of the ammonium salt with silver nitrate, the silver salt was obtained as a voluminous white pre-

cipitate, which, after being dried over sulphuric acid in a vacuum, gave the following numbers on analysis:

0.3050 gram substance gave 0.1147 gram Ag = 37.61 per cent.

Theory, $C_9H_7O_4Ag$ = 37.63

I hope at some future time to be able to examine more thoroughly this curious reaction, and if possible to determine the constitution of the body $C_9H_8O_4$.

Dibenzoylacetic Acid.

In the preceding chapters it has been shown that ethylic benzoylacetate is capable of forming derivatives in which the hydrogen-atoms of the methylene group are displaced by alcoholic radicles such as ethyl, allyl, etc., in exactly the same way as ethylic acetoacetate. It was thought likely that very interesting results might be obtained if the acid chlorides, such as benzoyl chloride, were substituted for the iodides of the alcoholic radicles in the above reaction. If the sodium compound of ethylic benzoylacetate be heated with benzoyl chloride, the ethyl salt of dibenzoylacetic acid is formed according to the equation,

$$C_6H_5.CO.CHNa.COOC_2H_5 + C_6H_5COCl = (C_6H_5.CO)_2CH.COOC_2H_5 + NaCl.$$

This ethereal salt on hydrolysis gives dibenzoylacetic acid,

$$(C_6H_5.CO)_2CH.COOH.$$

When boiled with dilute acids, dibenzoylacetic acid is easily split up into acetophenone, benzoic acid, and carbonic anhydride, thus,

$$(C_6H_5.CO)_2CH.COOH + H_2O = C_6H_5.CO.CH_3 + C_6H_5.COOH + CO_2.$$

If boiled with water, a second reaction takes place at the same time, by which dibenzoylmethane is formed according to the equation,

$$(C_6H_5.CO)_2CH.COOH = (C_6H_5.CO)_2CH_2 + CO_2.$$

Dibenzoylmethane.

In the preparation of ethylic dibenzoylacetate it is not necessary to use the pure dry sodium compound of ethylic benzoylacetate and act on it with benzoyl chloride in ethereal solution, as was done in the first experiments, but we may proceed in the way usually employed in such syntheses, that is, by mixing ethylic benzoylacetate with sodic ethylate, and allowing benzoyl chloride

to act directly on the product in the following way: 0.6 gram of sodium is dissolved in absolute alcohol, well cooled, and then mixed with 4 grams of ethylic benzoylacetate. 3 grams of benzoyl chloride are now added drop by drop, the whole being well cooled in a mixture of ice and salt. The reaction is very energetic, each drop of benzoyl chloride instantly producing a precipitate of chloride of sodium, and so much heat is developed that the alcohol will boil if a refrigerating mixture is not used. After all the benzoyl chloride has been added, the whole is warmed on a water-bath for about a quarter of an hour to insure the reaction being complete, and the greater part of the alcohol is distilled off; water is then added, and the product allowed to remain for some time, in order to insure the decomposition of any slight excess of benzoyl chloride. The watery liquid is next extracted with ether once or twice, the ethereal solution well shaken with carbonate of soda to remove benzoic acid, dried over potassium carbonate, and the ether distilled off. A thick dark brown oil remains behind. This was not further purified, although it is possible that by fractioning in a vacuum the ethylic dibenzoylacetate might be obtained in a pure state, as in the case of the ethyl- and allyl-benzoylacetates.

In order to obtain the free acid, the crude ethereal salt was hydrolysed by warming with an excess of alcoholic potash for about ten minutes on a water-bath. The mixture became dark colored, and on adding water almost all of it dissolved, forming a dark brownish solution; this when acidified deposited the crude dibenzoylacetic acid as a thick oil, which became nearly solid on agitating for a short time. The product was collected, well washed with water, and dissolved in as little boiling alcohol (80 per cent.) as possible. On cooling, the acid crystallised out in colorless nodules, and was easily obtained pure and free from benzoic acid by repeated crystallisation. On analysis the following numbers were obtained:

0.2257 gram substance gave 0.0925 gram H_2O and 0.5926 gram CO_2.

	Found.	Calculated, $C_{16}H_{12}O_4$.
C	71.61 per cent.	71.64 per cent.
H	4.55	4.48
O	23.84	23.88

This substance was therefore dibenzoylacetic acid,

$$(C_6H_5.CO)_2CH.COOH.$$

The acid melts at 109°. When rapidly heated in small quantities, some of it distils undecomposed, but the greater part is split up into dibenzoylmethane and carbonic anhydride according to the equation,

$$\underset{\text{Dibenzoylacetic acid.}}{(C_6H_5CO)_2.CH.COOH} = \underset{\text{Dibenzoylmethane.}}{CH_2(CO.C_6H_5)_2} + CO_2.$$

Dibenzoylacetic acid is sparingly soluble in water and cold alcohol, but easily so in hot alcohol, benzene, and ether. The solution in alcohol gives a dirty red coloration on the addition of ferric chloride. The acid dissolves in concentrated sulphuric acid, producing a yellow solution, which, however, becomes colorless on warming. It dissolves slowly in solutions of ammonia, sodic hydroxide, and sodic carbonate, and is reprecipitated on the addition of an acid. In order to obtain a neutral solution of the ammonium salt, the pure acid was dissolved in a slight excess of dilute ammonia, and then allowed to stand over sulphuric acid in a vacuum until the excess of ammonia had evaporated. The salt itself is very easily soluble in water; on boiling the solution carbonic anhydride is given off, and the smell of acetophenone becomes noticeable. Several of the salts of dibenzoylacetic acid were prepared by precipitating the solution of the ammonium salt with various reagents. The *silver salt* is obtained on adding a solution of nitrate of silver as a white curdy precipitate, sparingly soluble in water. For analysis, the substance was dried at 80°.

0.1154 gram substance gave 0.0327 gram silver.

	Found.	Theory. $(C_6H_5CO)_2CH.COOAg$.
Ag	28.34 per cent.	28.72 per cent.

A solution of cupric sulphate precipitates the *copper salt* as a light yellowish-green mass, which appears to be somewhat soluble in hot water and alcohol. Prolonged boiling, however, decomposes the salt, cupric oxide being precipitated. This copper salt dissolves easily in ammonia, yielding a beautiful blue solution. The *barium salt* is soluble in water, and is prepared by shaking the finely powdered acid with baryta-water and a little alcohol for some time. After precipitating the excess of baryta by passing carbonic anhydride and filtering, a solution of the salt is obtained, which, however, is partly decomposed by evaporation. The *zinc salt* is also easily soluble in water. With a solution of the ammonium salt, acetate of lead gives a white curdy precipitate of the *lead salt.*

With a solution of sulphate of nickel, the ***nickel salt*** is obtained as a light green precipitate soluble in excess of sulphate of nickel. Ferric chloride gives a brownish-red coloration with dilute solutions of the ammonium salt; with more concentrated solutions, however, the *ferric salt* is precipitated as a dirty reddish precipitate somewhat soluble in hot water. Ferrous sulphate gives the same reaction. Chloride of tin precipitates the ***tin salt*** as a heavy white mass sparingly soluble in water.

If dibenzoylacetic acid is mixed with alcoholic potash, a yellowish-green solution is formed which is decomposed by boiling, benzoic acid and a neutral body being formed. On distilling dibenzoylacetic acid with soda-lime it is split up into benzene and an oily substance, which appears to be acetophenone.

In order to obtain pure ethylic dibenzoylacetate, the pure acid was dissolved in absolute alcohol, and hydrogen chloride passed through the solution until it was thoroughly saturated, the whole being kept well cooled during the operation. On adding water, an oil was precipitated, which, on distillation, came over almost entirely between 205–220° as a colorless oil smelling strongly of ethyl-benzoate. The pure ether can easily be prepared, however, by decomposing the silver salt of the acid with ethylic iodide in ethereal solution. After filtering from the precipitated iodide of silver and evaporating on a water-bath, ethylic dibenzoylacetate remains behind as a thick colorless oil of a faint fruity odor; it does not solidify when cooled down to —10°.

Several experiments were next made in the hope of obtaining tribenzoylacetic acid by treating ethylic dibenzoylacetate with sodic ethylate and benzoyl chloride as expressed in the equation,

$$(C_6H_5.CO)_2CNa.COOC_2H_5 + C_6H_5.COCl = (C_6H_5.CO)_3C.COOC_2H_5 + NaCl.$$

In this way an almost colorless oil is obtained, which, however, is unfortunately completely split up on hydrolysis, nothing but benzoic acid being formed.

As it appeared probable that ethylic tribenzoylacetate was really formed in the first place, an experiment was very carefully made with pure ethylic dibenzoylacetate, and the product, freed from excess of benzoyl chloride and benzoic acid by shaking with dilute sodic carbonate, was dried over carbonate of potash and analysed.

	Found.	Theory. $(C_6H_5.CO)_2C.COOC_2H_5$.	Theory. $(C_6H_5.CO)_2CH.COOC_2H_5$.
C	74.19 per cent.	75.00	72.97 per cent.
H	4.91	5.00	5.41
O	21.00	20.00	21.62

This ethereal salt is a very thick yellowish oil, which unfortunately could not be made to crystallise. On boiling it with dilute sulphuric acid, acetophenone and a solid acid, probably benzoic acid, are formed. It dissolves in alcoholic potash and is reprecipitated on adding a few drops of water, whereas ethylic dibenzoylacetate is only precipitated from its solution in alcoholic potash on the addition of a much larger quantity of water.

Decomposition-products of Dibenzoylacetic Acid.

Dibenzoylmethane.

As dibenzoylacetic acid contains two carbonyl-groups, it seemed probable that interesting results might be obtained by carefully examining its decomposition-products. The acid was therefore treated with several reagents; first of all with dilute sulphuric acid in the hope of simply splitting off carbonic anhydride, and thus obtaining dibenzoylmethane according to the equation,

$$(C_6H_5.CO)_2CH.COOH = CO_2 + CH_2(CO.C_6H_5)_2.$$

The experiment was carried out in the following way: A mixture of pure dibenzoylacetic acid with an excess of dilute sulphuric acid (1 : 2) was heated for about five hours in a flask connected with a reflux condenser; at the end of this a test-tube containing baryta-water was fixed, to serve as a rough indicator both of the quantity of carbonic anhydride and the rate at which it was given off.

The acid soon began to decompose, and swam about in the liquid at first as a semi-solid mass, but later on in large oily drops, a considerable quantity of carbonic anhydride being evolved. At the end of the reaction, the contents of the flask, which smelt strongly of acetophenone, were subjected to distillation by steam; in this way a considerable quantity of a colorless oil passed over and was extracted by shaking with ether. On distilling off the ether and subsequent fractioning, nearly the whole of the residual oil passed over between 195–205°, and without doubt consisted of nearly pure acetophenone. In order to be certain it was shaken with a solution of orthonitrobenzaldehyde in dilute sodic hydroxide,

when a considerable quantity of indigo was precipitated after the mixture had been standing for some time.

On cooling, the residue in the flask deposited a quantity of glittering crystals which were collected and dried. They melted at 120° and showed all the properties of benzoic acid, with which they were no doubt identical.

Dibenzoylacetic acid is therefore decomposed by boiling with dilute sulphuric acid into benzoic acid, carbonic anhydride, and acetophenone according to the equation,

$$(C_6H_5.CO)_2CH.COOH + H_2O = C_6H_5.COOH + C_6H_5.CO.CH_3 + CO_2.$$

In repeating this reaction more carefully, it was noticed that if the boiling with sulphuric acid were stopped before all the dibenzoylacetic acid had been decomposed, a small quantity of a solid body, insoluble in sodic carbonate, could be isolated; when this is dissolved in alcohol and ferric chloride added, it gives a beautiful reddish-violet coloration. As, however, only very small quantities of this compound could be obtained by this method, several experiments were tried in order to improve the yield, and it was found that simple boiling with distilled water gave the desired result.

Pure dibenzoylacetic acid was boiled with water in a flask connected with a reflux condenser as long as carbonic anhydride continued to come off in any quantity (about 4–5 hours).

The acid melted slowly and sank to the bottom of the flask as a heavy, slightly brownish oil, which on cooling partially solidified, the liquid becoming filled with needles of benzoic acid. A dilute solution of sodic carbonate was now added, and the whole well shaken and allowed to stand for some time until all the benzoic acid had dissolved. After filtering and washing with water a small quantity of a semi-solid mass remained, smelling strongly of acetophenone; the latter can be roughly separated from the crystals by spreading them out on a porous plate or by pressing between blotting-paper. The crude product thus obtained was then dissolved in a little hot methyl alcohol, from which it crystallised on cooling in beautiful flat plates; these are easily obtained pure by recrystallisation.

The analysis gave numbers agreeing with the formula,

$$CH_2(CO.C_6H_5)_2.$$

0.1967 gram substance gave 0.0952 gram H_2O and 0.5772 gram CO_2.

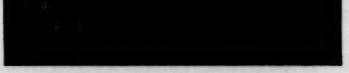
	Found.	Calculated, $CH_2(CO.C_6H_5)_2$.
C	80.03 per cent.	80.36 per cent.
H	5.37	5.36
O	13.60	14.28

This compound was therefore dibenzoylmethane or benzoylacetophenone. It melts at 81° and distils above 200°, apparently without the least decomposition. It is easily soluble in ether, alcohol, and chloroform, the alcoholic solution, on the addition of a drop of ferric chloride, giving an intense reddish-violet coloration which resembles very closely that produced by benzoylacetic acid itself. If the solution in hot methyl alcohol is cooled slowly, it crystallises most beautifully; it can, however, best be obtained in large crystals by allowing the ethereal solution to evaporate slowly. Professor Haushofer was kind enough to measure these crystals, and gave me the following description of them:

Crystalline system rhombic:

$$a : b : c = ? : 1 : 1.38.$$

Small crystals with rhomboidal base and extended in the direction of the makrodiagonal on which the surface oP (*c*), $\infty \breve{P}\infty$ (*a*), $\breve{P}\infty$ (*r*), and an undetermined makrodome, *d*, were observed. The only surfaces fit for measurement were *a*, *r*, and in some crystals *c*.



The surface *d* is smooth, curved, and appears only on one-half of the crystals (with respect to the basal section). The surface *c* is also generally curved.

	Measured.	Calculated.
$r : r$	108° 18′	...
$c : r$	125° 54′	125° 51′
$a : r$	90°	90°

The compound is remarkable by the strong dispersion in its axes. The medial line is the vertical axis. The makropinacoïd is the

plane of the optical axis for the red, and the brachypinacoïd for the blue. In the polariscope with white light, the surface *c* shows the interference figure of rhombic titanic acid (brookite).

Dibenzoylmethane is easily soluble in alkalis, particularly in alcoholic potash, and is reprecipitated unchanged on acidifying. It combines easily with phenylhydrazine, forming a solid substance, which, however, was not further examined.

Tribenzoylmethane.

Dibenzoylmethane, $CH_2(CO.C_6H_5)_2$, contains a methylene-group associated with two carbonyl-groups, and for this reason is soluble in alkalis, forming metallic salts, the methylene-group in this body behaving in exactly the same way as the corresponding one in ethylic benzoylacetate, $C_6H_5.CO.CH_2.COOC_2H_5$. It appeared probable, therefore, that by further treatment with sodic ethylate and benzoyl chloride a tribenzoylmethane might be formed according to the equation,

$$CHNa(CO.C_6H_5)_2 + C_6H_5.COCl = CH(CO.C_6H_5)_3 + NaCl.$$

This is in reality the case, as will be seen from the following experiment: 2 grams of pure dibenzoylmethane were mixed with a solution of 0.2 gram of sodium in absolute alcohol, and then as soon as all had completely dissolved, 1.4 gram of benzoyl chloride was added drop by drop. Sodic chloride was immediately precipitated, the mixture becoming warm. After all the benzoyl chloride had been added, the product was heated on a water-bath for about ten minutes to ensure the reaction being complete; a quantity of water was then added, when a solid body separated; this was collected, well washed with water, and spread out on a porous plate to remove a small quantity of oil adhering to the crystals.

The compound was easily purified by recrystallisation from alcohol, and gave the following numbers on analysis:

0.1849 gram substance gave 0.0864 gram H_2O and 0.5443 gram CO_2.

	Found.	Theory, $CH(CO.C_6H_5)_3$.
C	80.28 per cent.	80.49 per cent.
H	5.19	4.87
O	14.53	14.63

This substance, therefore, is tribenzoylmethane. On heating it melts at 224–225°, and sublimes at a higher temperature almost

without decomposition; in this respect it seems to be an extremely stable compound. Tribenzoylmethane is almost insoluble in cold alcohol, more easily soluble in hot, and crystallises from this solvent on cooling in small, almost microscopic, colorless needles. The hot alcoholic solution gives an orange coloration on adding a drop of ferric chloride. It is fairly easily soluble in benzene and carbon bisulphide, and crystallises in small needles on evaporating the solution. In chloroform and ether, on the contrary, it is sparingly soluble, and in light petroleum almost insoluble. It dissolves readily in alcoholic potash, and on adding water forms a colorless solution from which acids precipitate the original compound unchanged. On warming with concentrated sulphuric acid it is colored yellow. Nitric acid appears to entirely decompose it. Experiments were next made in the hope of obtaining tetrabenzoylmethane by the further action of sodic ethylate and benzoyl chloride on tribenzoylmethane, thus:

$$CNa(CO.C_6H_5)_3 + C_6H_5.COCl = C(CO.C_6H_5)_4 + NaCl.$$

By this means a small quantity of a colorless body was obtained which, after being extracted several times with boiling alcohol, melted between 260–270°, and gave the following results on analysis:

	Found.	Theory, $C(C_6H_4\overset{\frown}{C}O)_4$.	Theory, $CH(C_6H_5CO)_3$.
C	81.43 per cent.	80.58 per cent.	80.49 per cent.
H	5.15	4.63	4.87
O	13.42	14.80	14.63

As will be seen from the above, the analysis of such a substance does not show whether it is a tetra- or tri-benzoylmethane. The only fact which seems to prove that tetrabenzoylmethane had been formed is that the product is far more sparingly soluble in alcoholic potash than tribenzoylmethane. I hope at some future time to be able to continue the study of these interesting compounds, and if possible to improve the methods of preparing them.

Reduction of Ethylic Benzoylacetate.

Benzoylacetic acid being a ketonic acid, it was thought that it would be interesting to study the action of nascent hydrogen on it, in order, if possible, to obtain β-phenyllactic acid according to the equation,

$$C_6H_5.CO.CH_2.COOH + H_2 = C_6H_5.CH(OH).CH_2.COOH.$$

In this reaction it is better to use ethylic benzoylacetate than the free acid; the following method gives good results.

Ethylic benzoylacetate is dissolved in dilute sodic hydroxide solution, care being taken to avoid any large excess of alkali, and then 5 per cent. sodium amalgam is added in small portions at a time. The amalgam liquefies at first without evolution of hydrogen, the liquid becoming so warm that it is necessary to cool it continually. After about ten hours, hydrogen begins to be evolved, and the reaction is finished. The product is then filtered from a small amount of a resinous body (which will be described later on), the filtrate acidulated with dilute sulphuric acid, and extracted several times with ether. On distilling off the ether, an almost colorless oily acid remains, which does not solidify even after long standing in a vacuum over sulphuric acid. In order to purify it, the whole is converted into the barium salt by agitation with baryta-water, the excess of baryta removed by carbonic anhydride, and the precipitated barium carbonate filtered off. The colorless solution of the barium salt of the acid so obtained is acidified with hydrochloric acid, shaken several times with ether, and the ethereal solution dried over chloride of calcium. On distilling off the ether, a very thick colorless oil is left; and this, on standing for some time, solidifies almost completely, especially after scratching the sides of the vessel containing it with a sharp glass rod. It may be purified by crystallising it once or twice from benzene, when it is obtained in beautiful colorless nodules consisting of fine needles. It melts at 93–94°, and gave the following numbers on analysis:

0.2005 gram substance gave 0.1100 gram H_2O and 0.4760 gram CO_2.

	Found.	Theory, $C_6H_5.CH(OH).CH_2.COOH$.
C	64.75 per cent.	65.06 per cent.
H	6.09	6.03
O	21.16	28.91

The substance was therefore β-phenyllactic acid, and was further identified by an analysis of the silver salt, which is easily obtained by precipitating a neutral solution of the ammonium salt with nitrate of silver, as a white curdy precipitate, somewhat soluble in water.

0.3360 gram substance gave 0.1330 gram Ag = 39.58 per cent.

Theory, $C_6H_5.CH(OH).CH_2.COOAg$ = 39.56

On heating this silver salt it decomposes into silver carbonic anhydride and cinnamene, almost without charring. The acid itself, when carefully heated, splits up almost quantitatively into water and cinnamic acid, according to the equation,

$$C_6H_5.CH(OH).CH_2.COOH = C_6H_5.CH:CH.COOH + H_2O.$$

This acid has all the properties of the β-phenyllactic acid prepared by Glaser[1] by the action of sodium amalgam on phenylchlorolactic acid, $C_6H_5.CH(OH).CHCl.COOH$, its formation from ethylic benzoylacetate being a proof that the hydroxyl group is really in the β-position. The same acid is also formed by boiling phenylbromopropionic acid, $C_6H_5.CHBr.CH_2.COOH$, with water.[2]

By the action of nascent hydrogen on ethylic benzoylacetate there is always a certain amount of a resinous substance formed, which separates out of the alkaline solution during the reduction, and can easily be freed from the sodic salt of the β-phenyllactic acid by filtration and washing with water. As in some cases a considerable amount of this compound was formed, it was thought that it might contain something definite, and was therefore carefully examined. The filter-papers were extracted with ether, and the ethereal solution filtered and evaporated; by this means a very thick dark-brown oil was left behind, which, after standing for several days, partly crystallised. The crystals were easily obtained colorless and free from oil, by repeated washings with small quantities of ether in which they are difficultly soluble. Last of all they were dissolved in a little hot alcohol, from which they crystallise on cooling in thick colorless prisms melting at 102°.

The analysis gave the following result:

I. 0.1665 gram substance gave 0.0768 gram H_2O and 0.4581 gram CO_2.

II. 0.2082 gram substance gave 0.0906 gram H_2O and 0.5720 gram CO_2.

	Found.		
	I.	II.	Theory, $(C_9H_8O)_n$.
C	75.04	74.93 per cent.	75.00 per cent.
H	5.12	4.83	5.00
O	19.84	20.24	20.00

This substance therefore has the formula $(C_9H_8O)_n$, most likely $C_{10}H_8O_2$.

[1] Annalen **147**, 86. [2] Fittig and Binder, Annalen **195**, 138.

When warmed with alcoholic potash it yields an intense magenta-red solution; and on filtering and acidifying, a colorless crystalline acid is precipitated. The alcoholic solution does not give any color reaction with ferric chloride.

A small quantity of this body warmed with concentrated sulphuric acid dissolves, forming a pinkish solution with a slight greenish fluorescence. If, after standing for a short time, this solution be poured into water, a whitish amorphous substance separates; this forms an intense blue-green solution on the addition of an excess of sodic hydroxide. If the original substance, however, be more strongly heated with sulphuric acid, the pinkish color first produced becomes browner, and at last of a deep olive-green. On pouring this olive-green solution into water, a bright yellowish liquid is produced, which, on the addition of sodic hydroxide, becomes of a beautiful purple. This reaction is extremely delicate, and is produced by mere traces of substance. This compound is isomeric with a substance which was obtained by the action of sodium on acetate of phenyl, a reaction which W. R. Hodgkinson and I studied some time ago.[1] Curiously enough the latter also gives the same characteristic reaction when warmed with potash; the red color is destroyed, however, on diluting with water, which is not the case with the body described above.

Action of Phosphorous Pentachloride on Ethylic Benzoylacetate.

Geuther,[2] who was the first to study the action of pentachloride of phosphorus on ethylic acetoacetate, found that when it was treated with an excess of the former it was resolved into the chlorides of two isomeric chlorcrotonic acids, namely, β-chlor-α-crotonic acid, $CH_3.CCl:CH.COOH$, and the β-chloro-β-crotonic acid, $CH_3:CCl.CH_2.COOH$.

On decomposing these chlorides with water, and distilling with steam, the β-chloro-β-crotonic acid distils over first, and then the β-chlor-α-crotonic acid. As the methyl group of the ethylic acetoacetate must have taken part in the formation of β-chloro-β-crotonic acid, supposing the formula $CH_3:CCl.CH_2.COOH$ to be correct, it appeared interesting to repeat these experiments with ethylic benzoylacetate, in which the presence of the phenyl group would shut out the possibility of the formation of any acid analogous in constitution to β-chloro-β-crotonic acid.

[1] Journal of the Chemical Society. Transactions **37**, 487. [2] Zeitschr. f. Chem. 1871, 237.

In order to test this, 10 grams of ethylic benzoylacetate were dissolved in 25 grams of oxychloride of phosphorus, and 25 grams of phosphorous pentachloride slowly added. As the reaction appeared to take place very slowly at ordinary temperatures, the mixture becoming only slightly warm, the whole was heated for about half an hour on a water-bath, when the pentachloride slowly disappeared, hydrogen chloride being given off. As soon as the reaction was over the oxychloride of phosphorus was distilled off on a water-bath in a vacuum, the latter portions carrying over a small quantity of a crystalline substance which sublimed into the condenser in yellow needles; these, however, were not further examined. The residue, consisting of a dark-brown oil, was poured into ice-water and allowed to remain for some time, in order that acid chlorides and any excess of pentachloride of phosphorus might be entirely decomposed. An excess of sodic carbonate was then added, and the whole gently warmed with animal charcoal on a water-bath for about fifteen minutes, and filtered. On acidifying the filtrate, which was nearly colorless, it deposited a crystalline acid; this was collected, well washed, and recrystallised twice from alcohol. It was thus obtained perfectly pure in beautiful glittering plates, which, on analysis, gave the following result:

0.1798 gram substance gave 0.0665 gram H_2O and 0.3901 gram CO_2.

0.2424 gram substance gave 0.3080 AgCl.

	Found.	Theory, $C_9H_7O_3Cl$.
C	59.17 per cent.	59.18 per cent.
H	4.10	3.84
Cl	19.47	19.45
O	17.26	17.53

The compound was therefore chlorocinnamic acid, produced according to the equations,

I. $C_6H_5.CO.CH_2.COOC_2H_5 + 2PCl_5 = C_6H_5.CCl_2.CH_2.COCl + C_2H_5Cl + 2POCl_3$.

II. $C_6H_5.CCl_2.CH_2.COCl + H_2O = C_6H_5.CCl{:}CH.COOH + 2HCl$.

β-Chlorocinnamic acid.

By this reaction, therefore, β-chlorocinnamic acid should be obtained. There are two monochlorocinnamic acids known, the

α-monochlorocinnamic acid, $C_6H_5.CH:CCl.COOH$, and the β-monochlorocinnamic acid, $C_6H_5.CCl:CH.COOH$. These were obtained by Jutz[1] in a way exactly similar to that employed by Glaser[2] in the preparation of the monobromocinnamic acids, namely, by heating phenyldichloropropionic acid with potash:

$$\underset{\text{Phenyldichloropropionic acid.}}{C_6H_5.CHCl.CHCl.COOH} + 4KOH = \underset{\text{Potassic α-chlorocinnamate.}}{C_6H_5.CH:CCl.COOK} + \underset{\text{Potassic β-chlorocinnamate.}}{C_6H_5.CCl:CH.COOK} + 2KCl + 4H_2O.$$

He separated these acids by means of the potash salts, the salt of the α-acid being sparingly soluble in water, whereas the salt of the β-acid is easily soluble. The α-chlorocinnamic acid, crystallised from water, melts at 137–138°, crystallised from light petroleum at 142°. β-Chlorocinnamic acid melts at 114°. α-Chlorocinnamic acid is also formed by heating phenylchlorolactic acid with water at 120–200°:

$$\underset{\text{Phenylchlorolactic acid.}}{C_6H_5.CH(OH).CHCl.COOH} = \underset{\text{α-Chlorocinnamic acid.}}{C_6H_5.CH:CCl.COOH} + H_2O.$$

This is a proof that the chlorine is in the α-position, there being no doubt as to the constitution of phenylchlorolactic acid. A further proof of the constitution of α-chlorocinnamic acid is its formation by the action of acetic anhydride on a mixture of benzaldehyde with sodic monochloracetate, according to the equation,[3]

$$C_6H_5.COH + CH_2Cl.COONa = C_6H_5.CH:CCl.COONa + H_2O.$$

The chlorocinnamic acid obtained from ethylic benzoylacetate by the action of pentachloride of phosphorus in the way just described, melts at 142°, and possesses, strangely enough, all the properties of α-chlorocinnamic acid, with which it is no doubt identical, although, according to the equation given above, β-chlorocinnamic acid should be produced.

The formation of α-chlorocinnamic acid from ethylic benzoylacetate in this way is difficult to explain; one is forced to come to the conclusion that the β-acid is first formed, and afterwards, under the influence of such powerful reagents as pentachloride and oxychloride of phosphorus, that a molecular change takes place, whereby the β-acid is transformed into the α-acid. In the case of

[1] Berichte **15**, 788. [2] Annalen **143**, 330. [3] Plöchl, Ber. **15**, 1945.

the monobromocinnamic acids, the β-acid can with the greatest ease be transformed into the α-acid by distillation, or by heating with hydriodic acid, the change being almost quantitative. Still stranger is the fact that the β-monobromocinnamic acid on etherification is converted quantitatively into the ethyl salt of α-monobromocinnamic acid. This mobility of the bromine-atom makes it appear possible that these compounds are merely physical isomerides, and not chemical isomerides in the true sense of the word.

Condensation of Ethylic Benzoylacetate with Benzaldehyde.

The hydrogen-atoms of the methylene group in ethylic acetoacetate are very easily substituted by condensation with aldehydes, according to the equation,[1]

$$CH_3.CO.CH_2.COOEt + R.CHO = CH_3.CO.C(:CH.R).COOEt + H_2O.$$

This condensation is best brought about by mixing the ethylic acetoacetate with the calculated amount of the aldehyde, and then after cooling in a freezing mixture, saturating the whole with hydrogen chloride. After standing for about two days, the reaction is complete, the resulting product, *e.g.*, in the case of the condensation of ethylic acetoacetate with benzaldehyde, consisting of a mixture of two isomeric ethylic acetylbenzylchloracetates,

$$\begin{matrix} C_6H_5.CHCl \\ CH_3.CO \end{matrix}\!\!>\!CH.COOC_2H_5 \text{ and } \begin{matrix} C_6H_5.CH_2 \\ CH_3.CO \end{matrix}\!\!>\!CCl.COOC_2H_5,$$

which are easily separated by crystallisation from light petroleum. Both these compounds are decomposed by distillation, yielding hydrogen chloride and ethylic acetylbenzalacetate,

$$\begin{matrix} C_6H_5.CH \\ C_6H_5.CO \end{matrix}\!\!>\!C.COOC_2H_5.$$

Claisen explains this condensation by supposing that the aldehyde is first converted by the hydrochloric acid into an unstable chlorhydrol, R.CH(OH)Cl, which then acts on the ethylic acetoacetate in the following way:

$$R.HC\!<\!\begin{matrix} OH \\ Cl \end{matrix} + H_3C\!<\!\begin{matrix} CCO.CH_3 \\ COOC_2H_5 \end{matrix} = R.CHCl.HC\!<\!\begin{matrix} CO.CH_3 \\ COOC_2H_5 \end{matrix} + H_2O.$$

On substituting benzoylacetate for ethylic acetoacetate, it was found that condensation with aldehydes took place in precisely the

[1] Claisen, Annalen **218**, 170.

same way. As it appeared interesting to prove the analogy between ethylic benzoylacetate and acetoacetate in this respect also, the condensation of the former with benzaldehyde was further studied.

10 grams of ethylic benzoylacetate were mixed with 5 grams of benzaldehyde, and the whole, after being cooled below 0° in a freezing mixture, was completely saturated with hydrogen chloride. The product soon became very thick and milky, from the formation of minute globules of water, which, after standing for 24 hours at the ordinary temperature, settled out in large drops on the side of the vessel.

The dark brown oily product was dissolved in ether, well washed, first with water and then with sodic carbonate solution, to remove the excess of hydrochloric acid, and finally dried over potassic carbonate. After filtering and distilling off the ether, a dark brownish very thick oil remained; this was distilled as rapidly as possible under diminished pressure (200 mm.), only a small residue being left. The distillate, which was nearly colorless, was distilled again, under the same pressure, the first portions, consisting of acetophenone and unchanged benzaldehyde, being rejected; afterwards a thick oil came over, which rapidly solidified on standing. The latter was dissolved in hot methyl alcohol, from which on cooling it crystallised in beautiful colorless needles, easily obtained pure by recrystallisation.

The analysis of the crystals, dried at 70–80°, gave the following numbers:

I. 0.2243 gram of substance gave 0.1195 gram H_2O and 0.6321 gram CO_2.

II. 0.2022 gram of substance gave 0.1040 gram H_2O and 0.5665 gram CO_2.

	Found.		Theory. $C_6H_5.CO.C\lessgtr^{CH.C_6H_5}_{COOC_2H_5}$.
	I.	II.	
C	76.86	76.83 per cent.	77.14 per cent.
H	5.91	5.74	5.72
O	17.23	17.43	17.14

The compound is therefore ethylic benzalbenzoylacetate. Ethylic benzalbenzoylacetate crystallises from methyl alcohol in long colorless glittering prisms, which melt at 98–99°. It is pretty easily soluble in hot methyl alcohol, sparingly so in cold. Like ethylic acetylbenzalacetate, it crystallises very readily. It

separates from a mixture of benzene and light pretroleum in flat plates, which polarise light splendidly. It crystallises best, however, from ether. If the ethereal solution is allowed to evaporate slowly, the sides and bottom of the vessel containing it become covered with large transparent glittering prisms, which do not lose their lustre on drying. Professor Haushofer, who kindly measured some of the crystals, gave me the following description of them:

Crystalline system monoclinic:

$$a : b : c = 1.2730 : 1 : 0.7461. \quad \beta = 86° 36'.$$

Pale yellow lustrous crystals, forming the combinations $\infty P\infty\,(a)$, $\infty P(p)$, $-P\infty(r)$, $P\infty\,(s)$, extended in the direction of the ortho-

diagonal, often also tabular on the surface *a*. The surfaces of this zone are smooth, but as a rule indented, and the measurements are therefore somewhat irregular.

	Measured.	Calculated.
$p : p$	$= 103° 36'$	...
$r : p$	$= 190\ 37$	...
$s : r$	$= 119\ 20$	...
$r : a$	$= 122\ 57$	$122° 53'$
$p : a$	$= 128\ 30$	$128\ 12$
$s : a$	$= 117\ 53$	$117\ 47$
$s : p$	$= 106\ 40$	$106\ 45$

Ethylic benzalbenzoylacetate dissolves in sulphuric acid, producing a yellow solution, which, however, becomes colorless again on standing or gently warming. The solution of this body in chloroform is only very slowly attacked by bromine.

Several saponification experiments were next made, in the hope of obtaining benzylideneacetophenone, according to the equation,

$$C_6H_5.CH : C\begin{matrix}CO.C_6H_5\\ COOC_2H_5\end{matrix} + H_2O =$$
$$C_6H_5.CH : CH.CO.C_6H_5 + CO_2 + C_2H_5.OH,$$

but without result. When ethylic benzalbenzoylacetate was heated with dilute hydrochloric acid in a sealed tube at 160° for seven hours, it was decomposed in part, producing a yellow oil. On opening the tube, large quantities of carbonic anhydride escaped, and on fractioning the product a considerable amount was obtained boiling below 210°, and consisting of a mixture of benzaldehyde and acetophenone. The thermometer was then removed, and the residue distilled in a vacuum, when a thick oil came over, which solidified on cooling. After crystallisation from methyl alcohol it melted at 98°, and showed all the properties of ethylic benzalbenzoylacetate. Negative results were also obtained on boiling it with potash, only small quantities of benzoic acid being produced.

Claisen[1] obtained similar results on trying to obtain ethylideneacetone and crotonic acid by saponifying ethylic acetylethylideneacetate, $\begin{matrix}CH_3.CH\\CH_3.CO\end{matrix}>C.COOC_2H_5$, with potash, and attributes this to the fact of the latter class of bodies being so easily decomposed into their components, and thus giving only aldehyde and the decomposition-products of ethylic acetoacetate, respectively ethylic benzoylacetate on hydrolysis. Another method employed by Claisen to effect the condensation of aldehydes with ethylic acetoacetate was by heating a mixture of the two bodies in a sealed tube with acetic anhydride. In order to see whether this also took place in the case of ethylic benzoylacetate, 10 grams of the latter, 5 grams of benzaldehyde, and an excess of acetic anhydride, were heated together in a sealed tube at 180–200° for six hours. On opening the tube a large quantity of carbonic anhydride escaped. The product, which was a dark brown oil, was then directly fractioned. Below 100° a small quantity of a limpid oil came over, which, after washing and refractioning, distilled almost entirely between 70° and 80° as a light oil, smelling strongly of ethylic acetate. After the excess of acetic anhydride and acetic acid had distilled over, the thermometer rose rapidly to 180°, and between that and 210° a considerable quantity of a mixture of benzaldehyde and acetophenone came over. The residue was then distilled under diminished pressure, when the latter portions, which were collected separately, partially solidified on cooling. The crystals were first roughly freed from oily matter by spreading them out on a porous plate, and then purified by crystallisation, once from methyl alcohol and once from ether.

[1] Annalen **218**, 173.

The analysis gave the following numbers:

0.1863 gram substance gave 0.0976 gram H_2O and 0.5254 gram CO_2.

	Found.	Theory. $C_6H_5.CO \atop C_6H_5.CH > C.COOC_2H_5$.
C	76.92 per cent.	77.14 per cent.
H	5.82	5.72
O	17.26	17.14

The crystals melted at 98°, and the body was therefore ethylic benzalbenzoylacetate. The yield by this method was not nearly so good as by the one previously described. It is possible that the temperature employed (180–200°) was too high, and that some of the product was again resolved into its components, the ethylic benzoylacetate being further decomposed into acetophenone and carbonic anhydride.

ON RESACETOPHENONE.

By Arthur Michael and George M. Palmer.

Nencki and Sieber[1] have obtained a series of compounds by the action of anhydrous zinc chloride on mixtures of acetic acid and polyatomic phenols, which they considered as hydroxyl derivatives of acetophenone. The evidence in favor of this view is not very conclusive, as they found that resacetophenone — $C_6H_3 — \overset{(OH)_2}{CO — CH_3}$ —forms but a mono-acetyl derivative. This compound could be boiled for a long time with acetic anhydride without undergoing any change. Although the discoverers remarked that this result is somewhat surprising in view of the constitution they assigned to the compound, they have not given any further experimental support to it. It seemed to us that the formation, if correct, of but a mono-acetyl derivative makes it probable that only one hydroxyl exists in resacetophenone, as the above method is used by general consent to ascertain the number of hydroxyls in a compound, and no instance is known to us where the reagent has failed to replace all the hydrogen of the hydroxyl of alcohol radicles. One of us[2] has suggested the constitution $C_6H_4 \overset{O}{\underset{O}{}} C(OH)CH_3$,

[1] Journal für pr. Chemie [N. F.] **28**, 147.

[2] A. Michael, this Journal, 1883, 94.

which is certainly more in conformity with the formation of a mono-acetyl derivative. The following experiments were made with a view of ascertaining which of these two constitutional formulæ is correct. E. Fischer has shown that phenylhydrazine acts on ketones and aldehydes with the elimination of water, and that the reagent may be used to characterise these classes of compounds. For the purpose of ascertaining whether resacetophenone contains a carbonyl, an alcoholic solution of that substance and phenylhydrazine was allowed to stand for a day, and then the alcohol driven off. The crystalline compound that remained was purified by crystallisation from xylene and analysed with the following result:

0.4655 gram of substance gave 50.5 cc. of N, at 26.5°, and 762 mm.

	Theory for $C_6H_3\overset{(OH)_2}{C-CH_3}N_2HC_6H_5$	Found.
N	11.6	12.1

The compound forms large prismatic plates that melt at 159°. It is insoluble in hot water, soluble in hot alcohol and benzene.

This result is evidently strong evidence of the presence of carbonyl in resacetophenone, and therefore that the constitution suggested by Nencki and Sieber is correct. We deemed it desirable, however, to confirm Nencki and Sieber's results on the action of acetic anhydride on resacetophenone.

A solution of twenty grams of resacetophenone in sixty grams of anhydride was heated to simmering for one hour and then fractionated. As soon as the anhydride had passed over the thermometer rose rapidly to 303°, at which temperature the acetyl-compound passed over. The crystalline distillate was crystallised several times from absolute alcohol. On analysis the following results were obtained:

0.3610 gram of substance gave 0.8210 gram of CO_2 and 0.1655 gram of H_2O.

0.3601 gram of substance gave 0.8175 gram of CO_2 and 0.1648 gram of H_2O.

	Theory for $C_6H_3\overset{OOCCH_3}{OH}\overset{}{COCH_3}$	Theory for $C_6H_3\overset{OOCCH_3}{OOCCH_3}\overset{}{COCH_3}$	Found. I.	Found. II.	Nencki & Sieber.
C	61.85	61.06	62.0	61.9	61.61
H	5.15	5.08	5.1	5.08	5.38

Our compound agreed in its properties with those given by Nencki and Sieber, except that it melted at 74° instead of at

72°. These results confirm those of Nencki and Sieber that an excess of acetic anhydride only forms the mono-acetyl derivative of resacetophenone, and that the compound shows an anomalous behavior in this respect. We endeavored to obtain the diacetyl-compound by heating the compound with a mixture of anhydride and dry sodium acetate, as Lieberman has shown that this mixture always forms the highest possible acetyl derivative, but did not obtain products that could be brought into a state suitable for analysis.

Nencki and Sieber[1] mention that their attempts to obtain a hydroxyacetophenone by the action of zinc chloride on a mixture of phenol and acetic acid were without success. We have succeeded, by increasing the proportion of zinc chloride, in obtaining the compound.

Twenty grams of phenol, thirty grams of glacial acetic acid and thirty grams of zinc chloride were heated for about an hour to incipient boiling, and the product then thrown into water. The mixture was boiled until the excess of phenol was expelled; and, on cooling, long needles were deposited on the bottom of the beaker, and some were also contained in the resin that floated on the water. They were separated as far as possible and then crystallised several times from moderately strong chlorhydric acid, by which process they were freed from zinc chloride. The crystals before treating with chlorhydric acid contained a considerable percentage of zinc, and were probably a double compound of the phenol with zinc chloride. For analysis the substance was crystallised several times from dilute alcohol.

0.2645 gram of substance gave 0.6814 gram of CO_2 and 0.1381 gram of H_2O.

	Theory for $C_6H_4{<}^{OH}_{CO-CH_3}$.	Found.
C	70.6	70.3
H	5.8	5.79

The compound crystallises in long prismatic needles, resembling those of phthalic anhydride, or short prisms melting at 108°. It is insoluble in hot water, but soluble in hot chlorhydric acid, separating out of the solution as it cools. In alcohol it is quite soluble. The yield obtained was very small, as the decomposition appears to proceed further with the formation of a resinous substance.

TUFTS COLLEGE, MASS.

[1] Journal für pr. Chemie (N. F.) **23**, 346.

ON INACTIVE ASPARTIC ACID.

By Arthur Michael and John F. Wing.

At the time when Dessaignes[1] discovered the artificial formation of inactive aspartic acid from ammonium malate the first compound was considered as the acid amide of the other; and its synthesis, although of considerable interest, was in accordance with the general reaction of amide-formation from ammonium salts of organic acids by heating. The reaction became of far greater interest when Kolbe interpreted aspartic acid as amidosuccinic acid, as it then showed itself to be without precedent. There is no doubt that the formation of aspartic acid from ammonium malate is preceded by the elimination of water, forming either malate or fumarate, as Dessaignes[2] has shown that it may be obtained from the product formed by the action of heat on either of these compounds. The further stage of the reaction is probably very complicated, and it is an unsettled question whether the amorphous product which yields aspartic acid on continued treatment with boiling chlorhydric acid, is identical with the product obtained in the action of heat on asparagine. Artificial aspartic acid, as is well known, differs in its properties very considerably from those of the natural acid. Not only is it optically inactive, but it differs also in its crystalline form, its solubility in water; and, also, several of its salts have an entirely different form from those of the natural acid.

Such differences in properties between optically active and inactive isomers are not uncommon, although those between the compounds in question are unusually large, sufficient to make us closely examine the reasons for accepting Dessaignes' compound as amidosuccinic acid. This view rests altogether on the basic properties of the compound and its conversion by Pasteur[3] into optically inactive malic acid, but neither of these reasons can be considered as offering conclusive evidence for its constitution, especially in view of the peculiar formation of the compound.

We have endeavored to prove the constitution of inactive aspartic acid indirectly; that is, to convert the active acid into the inactive form and compare the product thus obtained with Dessaignes' compound.

[1] Compt. Rendus **30**, 324; **31**, 432. [2] *loc. cit.* [3] Ann. chim. phys. [3], **34**, 30.

It was found that this result was best attained by heating a dilute chlorhydric acid solution of the natural acid in closed tubes. At 100° it was found that continued heating for several days failed to cause the acid to lose its optically active properties: equally fruitless was it to heat the tubes under 160°, but heating at 170–180° for several hours sufficed to change the acid completely into the optically inactive modification. It is necessary to keep pretty closely within these limits of temperature, as at 200° the acid undergoes a complex decomposition and the contents of the tubes became quite dark in color. The contents of the tubes that had been heated to 170–180° were evaporated to dryness on a water-bath, and the acid separated according to the method given by Dessaignes. An analysis of the acid gave the following numbers:

0.269 gram of acid gave 0.3575 gram of CO_2 and 0.1283 gram of H_2O.

	Theory for $C_2H_3NH_2(COOH)_2$.	Found.
C	36.09	36.21
H	5.26	5.40

This acid agrees in all its properties with the acid obtained by treating the compound from ammonium malate with boiling nitric acid. Like that acid it crystallises in small monoclinic needles. A comparison of solubilities of this inactive acid and Dessaignes' acid gave further proof of the identity of the two products. The results, obtained by the method of V. Meyer, were as follows:

	Inactive aspartic acid by heat.	Inactive acid from ammonium malate.
At 7° C.	one part acid soluble in 238 pts. H_2O	235.9 pts. H_2O
At 5°	" " " 224.5 " " "	223.8 " " "
At 7°	" " " 238 " " "	236 " " "

The hydrochloric acid salt of the natural acid crystallises in rhombic plates, while the same salt of Dessaignes' acid crystallises in monoclinic prisms. It was found that the salt of the natural acid rendered inactive also crystallises in similar monoclinic crystals. A further difference exists between the crystalline forms of the sodium salts, that of the active acid belonging to the rhombic, and the salt of Dessaignes' acid to the monoclinic. In this case, also, the identity of the inactive acids showed itself. We believe that these results show quite conclusively that Dessaignes' acid is really amidosuccinic acid; in fact, the optically inactive modification of the natural acid. In regard to its formation from acid

ammonium malate, it may be supposed that the acid amide of fumaric or maleic acid is formed as the first stage of the reaction,[1] and that this compound passes over into the lactimide of aspartic acid, or some derivative of it formed by elimination of water; a reaction which would be somewhat similar to the formation of the lactone of β-oxycarboxylhydrocinnamic acid from carboxylcinnamic acid by heating:

$$\begin{array}{l} CH-CONH_2 \\ | \\ CH-COOH \end{array} = \begin{array}{l} NH \\ CH< \quad | \\ \quad\ CO \\ CH_2-COOH \end{array}$$

$$C_6H_4 \begin{array}{l} CHCHCOOH \\ \\ COOH \end{array} = C_6H_4 \begin{array}{l} CH< \quad CH_2.COOH \\ \quad\ CO> O \end{array}$$

We have attempted to prove the formation of amido acids by heating the acid ammonium salts of unsaturated polybasic acids, but without obtaining any success. Neither from ammonium citraconate, mesaconate, nor tricarbyllate could a basic product be obtained.

It seemed possible that by heating acid aniline malate, and treating the condensation-product with mineral acids, phenylamidosuccinic acid, or a quinoline derivative, might be obtained, and for this reason the experiment was made. Malic acid and aniline, in the proportion of equal molecules, were heated in a water-bath for several hours, then brought into a retort and heated gradually in a paraffine bath up to 230–250°. At first water was driven off, then long yellow needles sublimed into the neck of the retort, and a dark-colored residue remained behind. The yellow sublimate was purified by several crystallisations from water, and gave the following results on analysis:

0.2872 gram of substance gave 0.7642 gram of CO_2 and 0.1262 gram of H_2O.

0.1484 gram of substance gave 18 cc. of nitrogen at 21° and 750 mm.

	Theory for $C_9H_8\begin{matrix}CONHC_6H_5\\COOHC_6H_5\end{matrix}$	Found.
C	72.10	72.55
H	5.26	4.86
N	9.86	10.19

The substance crystallises from water as slender yellow needles, often three or four inches in length. It melts at 87°.5.

[1] The compound formed by heating acid ammonium malate is still called fumarimide. This name should disappear, as the compound evidently is not a derivative of fumaric acid.

By continued boiling with water it decomposes into fumaric acid and aniline, a decomposition that proceeds much faster when it is boiled with chlorhydric acid. The substance is evidently the anilide of fumaric acid.

The dark residue remaining in the retort was insoluble in water; soluble with difficulty in alcohol. It was soluble in alkalis, and after the solution has been heated acid gave a precipitate which proved to be fumaric acid. No basic compound other than aniline could be isolated from it.

TUFTS COLLEGE, MASS.

REVIEW.

LEHRBUCH DER ALLGEMEINEN CHEMIE. Erster Band: Stöchiometrie. Von DR. WILH. OSTWALD, Professor am Polytechnikum zu Riga.

This book furnishes fresh evidence of the increased attention which the subject commonly called physical chemistry is attracting. The object of the book is to present in an orderly way the results which have been reached in investigating chemical action as such. It is not a treatise on chemical substances, but it has reference to the way in which chemical substances act upon one another, and to the fundamental hypotheses of the science of chemistry. The first volume deals with the subject of stoichiometry in its broadest sense, everything of importance that has any connection with the problem of determining atomic weights being discussed.

In the second chapter the results of the author's own recalculations of the atomic weights are given. In discussing these results he, of course, gives a passing consideration to Prout's hypothesis, and rather summarily disposes of it in these words: "Stas's results having been shown to be correct, the fate of Prout's hypothesis in its original form is finally decided—it is false."

The second book is entitled "Stöchiometrie gasförmiger Stoffe." Under this head are treated the phenomena of gases, so far as these are of importance in connection with the subject of atomic weights. The law of Gay Lussac and the hypothesis of Avogadro, the kinetic theory of gases, the specific heat of gases, and the optical properties of gases are the subjects of the chapters which make up the second book.

The third book is entitled "Stöchiometrie der Flüssigkeiten." This includes such subjects as volume relations of liquid substances,

solutions, refraction of light by liquids, rotation of the plane of polarisation, capillarity, diffusion and osmose, and the specific heat of liquids.

Under the head of "Stöchiometrie fester Körper," which is the title of the fourth book, the following subjects are taken up: the general properties of solid bodies, volumes of solid bodies, crystals, isomorphism and polymorphism, optical properties of solid bodies, changes in the state of aggregation, specific heat and adsorption.

Finally, in the fifth and last book of the first volume, the general subject "Systematik" is treated. The special subjects are: the choice of atomic weights, the periodic law, the molecular theory, and the theory of chemical compounds.

The book is characterised by great clearness, and the recognition of the boundary between the region of facts and that of hypothesis. In his preface the author says: "In preparing my book I have constantly kept in mind the necessity of carefully separating the observed facts from hypotheses and theories. To the former I have given their fullest value, the latter I have properly represented as the result of experience and limited by it.

"I may perhaps hope that by so doing I have rendered a service at this time, when the accusation is made against the present direction of chemistry, and frequently with justice, that hypotheses are confused with facts."

Of the periodic law the author speaks very highly. He considers that the recognition that the properties of the elements are periodic functions of their atomic weights, is one of the most important advances made in the science of chemistry in recent times. Every attempt to find similar comprehensive regularities when other atomic weights were used than those now commonly accepted has been a complete failure, so that the periodic law deserves to rank with isomorphism, and with the law of Dulong and Petit and of Avogadro, as furnishing a reliable means of determining atomic weights.

There is no book which gives a more satisfactory treatment of the subjects taken up than this does. Its careful study cannot fail to aid the student to think clearly and to secure a firm foundation for his thoughts. I. R.